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Thermal Regeneration of Activated Carbon

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Thermal Regeneration Of Activated Carbon

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16. ABSTRACT

A three-part experimental study of activated carbon adsorption and thermal regeneration has been completed. The project included an experimental pilot plant thermal regeneration study to determine specific thermal regeneration characteristics of selected petrochemical waste materials and a low-pressure thermal investigation. Results of these studies showed: (1) Small polar molecular species, or species highly soluble in water, are resistant to carbon sorption. (2) Extreme acidic or basic waste streams may require pH adjustment to promote carbon sorption. (3) Batch isotherm values provide basic information relative to activated carbon-petrochemical waste column design. (4) Vacuum regeneration of petrochemical saturated activated carbon is effective and efficient. With most sorbent-sorbate combinations tested, the carbon sorbent could be regenerated to 95% of original sorption capacity. (5) Temperature required for carbon regeneration was a function of waste type (composition) and sorption capacity.

The report describes experimental methods of differential thermal analysis, vacuum thermal regeneration, isotherm and column derived sorption values, and quantitative relationships of temperature and thermal regeneration response.

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THERMAL REGENERATION OF ACTIVATED CARBON

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FOREWORD

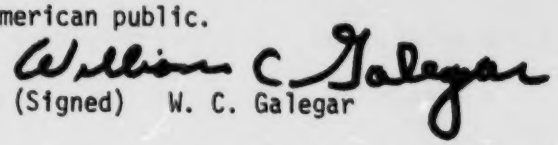
The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows, (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries, and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.



(Signed) W. C. Galegar

ABSTRACT

A three part experimental study of activated carbon sorption and thermal regeneration has been completed. The initial plan of this study predicated that two 1 gallon-per-minute flow capacity pilot-plants would be fabricated and used to collect samples of petrochemical waste stream organic materials in the Baton Rouge, Louisiana area. Samples of the pilot-plant sorbent (activated carbon saturated with petrochemical waste) were to be used in an experimental thermal regeneration study. The purpose of the thermal regeneration experimental study was to determine the specific thermal regeneration characteristics of the petrochemical waste saturated activated carbon sorbent. Time requirements requisite to fabrication, operation, and maintenance of the sorption pilot-plants prompted revision of the initial study plan. Appropriate to the revised plan, two 1 gallon-per-minute pilot plants were fabricated and provided for operation. In addition, a laboratory study of the specific sorption characteristics of selected petrochemical waste materials, via batch isotherm and flow columns, was completed along with a low pressure thermal regeneration investigation.

Results of these studies showed:

1) Small polar molecular species, or species highly soluble in water, are resistant to carbon sorption.

2) Extreme acidic or basic waste streams may require pH adjustment to promote carbon sorption.

3) Batch isotherm values provide basic information relative to activated carbon-petrochemical waste column design.

4) Vacuum regeneration of petrochemical saturated activated carbon is effective and efficient. With most sorbent-sorbate combinations tested, the carbon sorbent could be regenerated to 95 percent of original sorption capacity.

5) Temperature required for carbon regeneration was a function of waste type (composition) and sorption capacity.

The report describes experimental methods of differential thermal analysis, vacuum thermal regeneration, isotherm and column derived sorption values, and quantitative relationships of temperature and thermal regeneration response.

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SECTION I

INTRODUCTION

The hydrocarbon based petrochemical industry in the United States is relatively young. Essentially this industry was initiated during the World War I era (ca. 1918-1920) and showed a relatively stable growth and development during the 1920-1940 period. The petrochemical industry expanded dramatically during World War II for the production of synthetic rubber and plastic materials. Following World War II the industry expanded rapidly, a five fold increase in production during the period from 1945 to 1960. The factors contributing to rapid expansion of the petrochemical industry were: favorable economic conditions, availability of economical and abundant supplies of petroleum raw material, and popular demand for the finished products, particularly synthetic fabric and plastic materials.

Generally, petrochemical production plants were located in geographical areas near petroleum production. Consequently, the highest density of petrochemical plants are found in the coastal regions of southern California and the gulf coast portion of Texas and Louisiana. Approximately 80 percent of the United States petrochemical production plants are located in the gulf coast between New Orleans, Louisiana, and Brownsville, Texas.

One of the problems common to many rapidly developing industries is waste treatment and disposal. This problem is not unique to the petrochemical industry; however, the dominant characteristic of the petrochemical industry - the continuous expansion and increasing variety of products and wastes produces - is unique. The basic characteristics of petrochemical wastes have been established; however, recent findings, relative to the potential biological hazards of petrochemical waste products, shows that more comprehensive knowledge about production, nature, and specific composition

of wastes must be developed. Concurrent with this demand is the associated application - developing effective methods of waste treatment. Petrochemical wastes, a common category, includes an ever expanding list of compounds, materials and mixtures. Because of this variety, it is necessary to consider each waste component on a molecular basis. Many of the components in petrochemical waste streams are present in low concentration - yet the chemical and physiological significance of these low concentration waste components must be considered. Many of the low concentration organic components in petrochemical waste exhibit low dose toxicity effects and are subject to biomagnification in the environment.

Ecologically, petrochemical wastes constitute a major hazard since waste materials contain relatively large amounts of non-biodegradable and toxic materials which may be discharged continuously. The latter factor is particularly important. Slow continuous discharge of a pollutant may produce a subtle change in the environmental structure, or response, which predisposes significant alteration of biota. The most direct evidence for this situation in man would be increased incidence of cancer and genetic anomalies.

One method of waste treatment which has direct application to petrochemical waste treatment is activated carbon sorption. Activated carbon is an established waste water treatment reagent which has been used extensively in the water treatment and waste water treatment industries. Activated carbon is a scavenging sorbent which exhibits broad range sorption affinity and high capacity for many organic and inorganic materials. In addition, activated carbon is readily availabe in granular form which can be incorporated into sorption columns for continuous on stream utilization.

The basic interest in this study was directed toward determination of

activated carbon sorption affinity and capacity for petrochemical wastes and evaluation of thermal regeneration response. These factors are relevant to the effectiveness and efficiency of the activated carbon sorption process and are requisite to design of waste treatment facilities.

Tentatively, the study program planned for this investigation envisioned a three-step sequence: design and fabrication of two 1 gallon-per-minute activated carbon pilot plants; application of the pilot plant to the Baton Rouge, Louisiana area petrochemical plant waste streams; and laboratory evaluation of activated carbon thermal regeneration. Time required for construction and maintenance of the sorption pilot plants was greater than expected and a revised schedule of study was developed. In the revised program, the pilot plant operation was conducted as a separate independent study. The balance of the investigation was conducted in the laboratory.

The basic objectives of this investigation were:

1) To design and construct two one-gallon-per-minute activated carbon sorption pilot plant units for application to petrochemical waste streams in the Baton Rouge, Louisiana area.

2) To determine the sorption affinity and capacity of various commercially available activated carbons for representative samples of petrochemical waste materials, and

3) To determine the thermal regeneration characteristics of spent activated carbon - petrochemical waste mixtures.

4) To determine the effectiveness and application of differential thermal analysis (DTA) for detailing thermal reactions of activated carbon experienced during low-pressure regeneration.

SECTION 2

CONCLUSIONS

Results of the vacuum thermal regeneration study show that vacuum thermal regeneration of activated carbon-waste sorbate samples proceeds as an exponential regeneration response. Generally, the minimum temperature required for regeneration threshold temperature is characteristic of the waste sorbate-sorbent combination.

The dominant factors influencing vacuum thermal regeneration response were identified experimentally as sorbate nature, sorption loading and temperature. The specific influence of each factor was determined separately and collectively. Results of these studies showed that:

1) Vacuum thermal regeneration of activated carbon-sorbate samples is effective for a wide variety of sorbates.

2) The nature of the sorbate, in terms of thermal degradation and volatility, determines the rate of regeneration response.

3) The specific differences in carbon sorbents do not significantly influence regeneration response.

4) The dominant factors which influence regeneration response are specific sorption capacity and temperature.

5) The general response pattern can be described by $Re = KT^n$.

The above relationships are significant because the specific influence of temperautre and loading are identified as major factors. Since the basic experimental values used in this study were derived from static experiments, using equilibrium temperature data and vacuum conditions, cognate factors such as heat transfer rate and mass transfer rates were not relevant.

Activated carbon can be regenerated under vacuum conditions. Experimental results developed in this study showed that vacuum regeneration, per se, is effective in restoring activated carbon sorption properties. This finding indicates that the carrier gases used in conventional thermal

regeneration are probably not requisite to thermal regeneration but serve to implement heat and mass transfer and control oxidation.

Results of the petrochemical waste-activated carbon sorption study showed that:

1) The process of adsorption on activated carbon is not uniformly effective for all petrochemical waste components particularly those small short chain highly oxygenated organic compounds.

2) Adsorption depends on the nature of the components of the waste, and in general, as the average molecular weight increases better adsorption occurs.

3) No one carbon exhibited the best results, and the choice of carbon depends on the waste as well as the waste concentration range.

4) The Freundlich Isotherm Model described the process of adsorption in petrochemical waste more accurately than the Langmuir or BET.

5) In the column study the characteristic breakthrough curve was exhibited by only the waste which exhibited a favorable adsorption pattern.

6) For a waste that exhibits a favorable adsorption pattern the optimum temperature of regeneration is in excess of 1000°F; whereas, for a waste that exhibits an unfavorable adsorption pattern it is much lower, in the order of 500°F.

7) Optimum temperature of regeneration must be established for each carbon-waste mixture.

8) Independent investigation of activated carbon by differential thermal analysis (DTA) established that DTA is a practical and useful analytical tool. Specifically, the results of the DTA study showed that: special techniques are required for development of realistic thermograms; low pressure degassing is necessary for removal of sorbed oxygen; and each activated carbon-sorbate system exhibits a unique thermal regeneration response.

SECTION 3

RECOMMENDATIONS

Regeneration of waste water sorbents will become an important part of the cost of waste treatment. Sorbent removal of dissolved organic and inorganic pollutants will probably become a popular or standard design practice and the cost of recharging the sorbent may well determine the applicability of sorption removal. Activated carbon is the most popular waste water treatment sorbent, yet its application is limited and the cost of regeneration is relatively high. Results presented in this study show that vacuum regeneration of activated carbon is promising. Potentially, vacuum regeneration of activated carbon could be achieved in place. This feature would probably reduce the cost of handling and shipping. In addition, there is some experimental evidence that shows that vacuum thermal regeneration might be less expensive than conventional multiple hearth furnace or rotary kiln regeneration.

Further study of the basic factors involved in carbon regeneration are required.

SECTION 4

DESIGN AND CONSTRUCTION OF SORPTION PILOT PLANTS

Determination of sorption affinity and capacity is the first step effort requisite to design of full scale activated carbon wastewater treatment facilities. Usually the activated carbon-waste affinity and sorption capacity are determined by small-scale laboratory tests using batch isotherm and column study techniques; however, the nature of petrochemical waste streams usually warrant direct onstream evaluation. Many of the petrochemical waste streams, common to production facilities, contain volatile compounds, are aggressively corrosive, and change composition rapidly. In an attempt to minimize these problems and provide a realistic evaluation of the activated carbon system, two one-gallon-per-minute activated sorption pilot plants were designed, constructed, and readied for field application.

The activated carbon sorption pilot plants designed and constructed for this study, Figure 1, consisted of four "Lucite" columns connected with plastic tubing. A pH monitoring flowthrough chamber and temperature probe were located in series with the 1/4 H.P. centrifugal pump. The pilot plant was designed to be operated in upflow or downflow condition. A picture of the assembled pilot-plant ready for operation is shown in Figure 4.

The assembled pilot-plants were operated in the laboratory at various flow rates, and activated carbon loadings, to determine hydrualic characteristics. Results of this study are presented in Table 1 and Figures 2 and 3. A description of the pilot plant components are listed below.

TABLE 1

FLOW RATE VS. PRESSURE VALUES FOR EXPERIMENTAL SORPTION PILOT PLANT

Column No.					
0	1	2	3	4	Flowrate (gpm)
Pressure Gauge Reading (psi)					
Sheave size 6" x 2 1/2" Belt 20"					
3.0	0.0	0.0	0.0	0.0	0.97
7.0	5.0	3.8	2.5	1.2	0.94
12.5	11.0	10.0	9.0	8.0	0.94
18.5	17.0	16.0	15.0	14.0	0.92
Sheave size 6" x 1 1/2" Belt 19"					
1.0	0.0	0.0	0.0	0.0	0.70
9.5	7.8	7.2	6.5	6.2	0.69
17.5	16.2	15.6	15.0	14.5	0.69
Sheave size 12" x 2 1/2" Belt 43"					
1.0	0.0	0.0	0.0	0.0	0.73
4.0	1.2	0.6	0.2	0.0	0.70
8.2	6.5	6.0	5.2	5.0	0.69
15.0	13.2	13.0	12.2	11.9	0.64
18.5	17.5	16.7	16.2	15.8	0.60
Sheave size 12" x 1 1/2" Belt 43"					
0.2	0.0	0.0	0.0	0.0	0.39
4.7	2.4	1.9	1.3	1.2	0.28
7.9	6.6	6.2	5.8	5.6	0.23
14.0	13.0	12.7	12.2	12.0	0.13

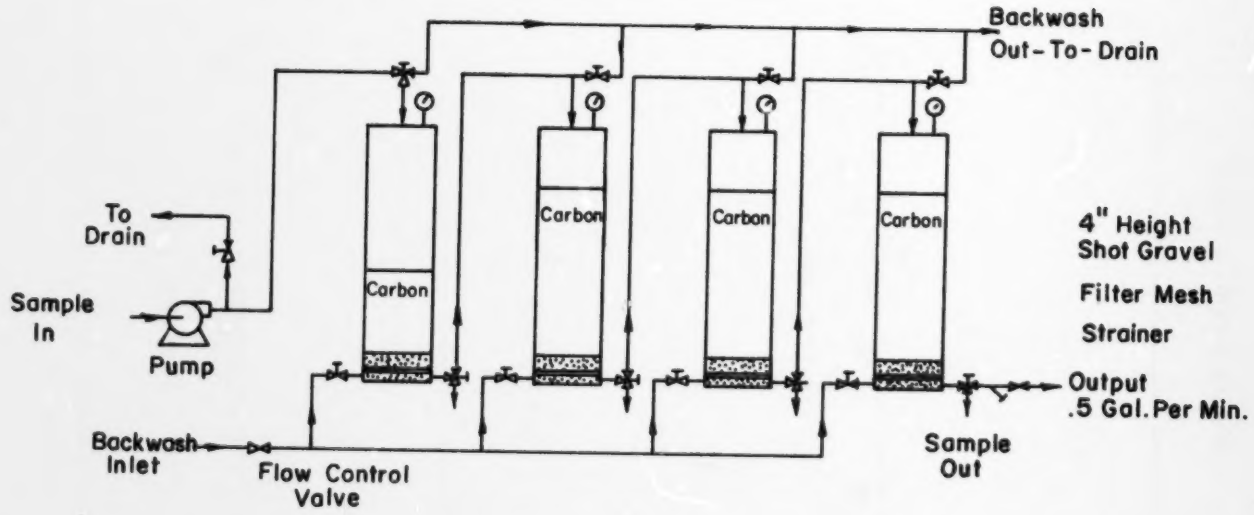


Figure 1. Block diagram of activated carbon sorption pilot-plant showing flow directions and valve locations.

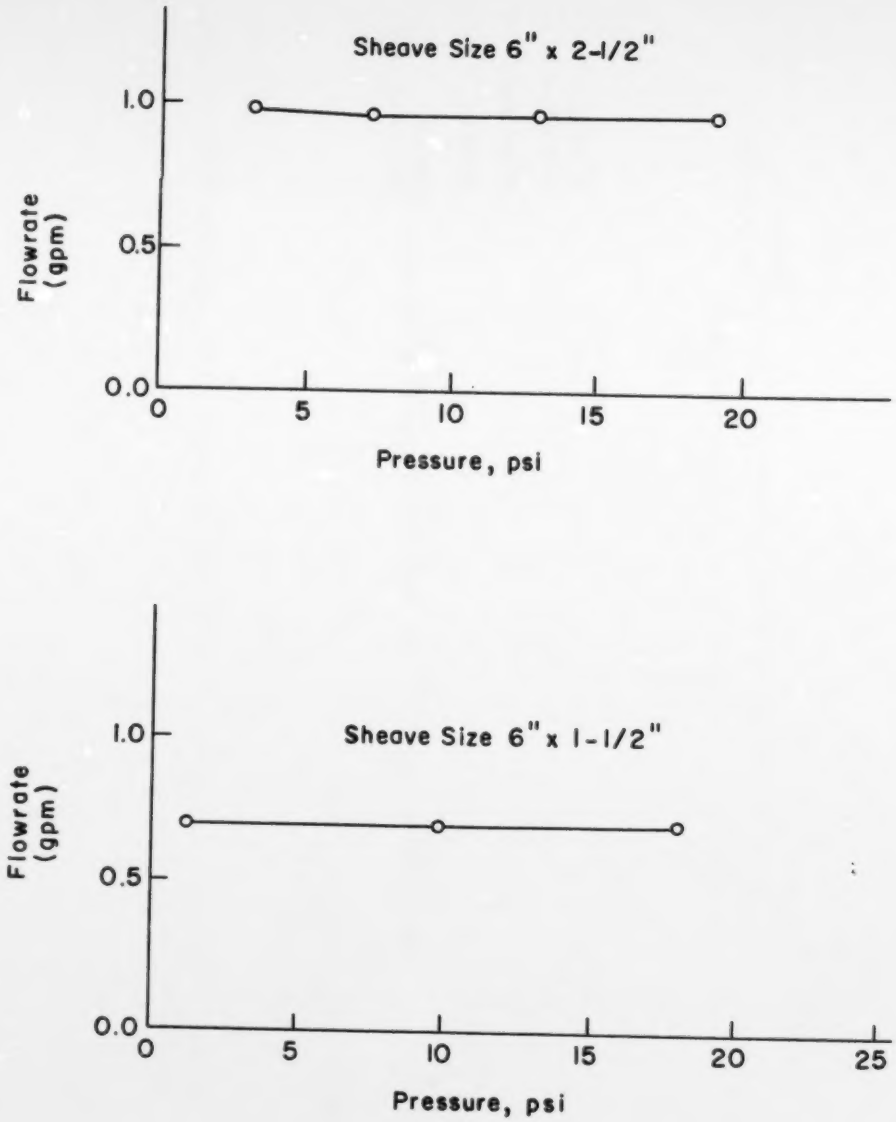
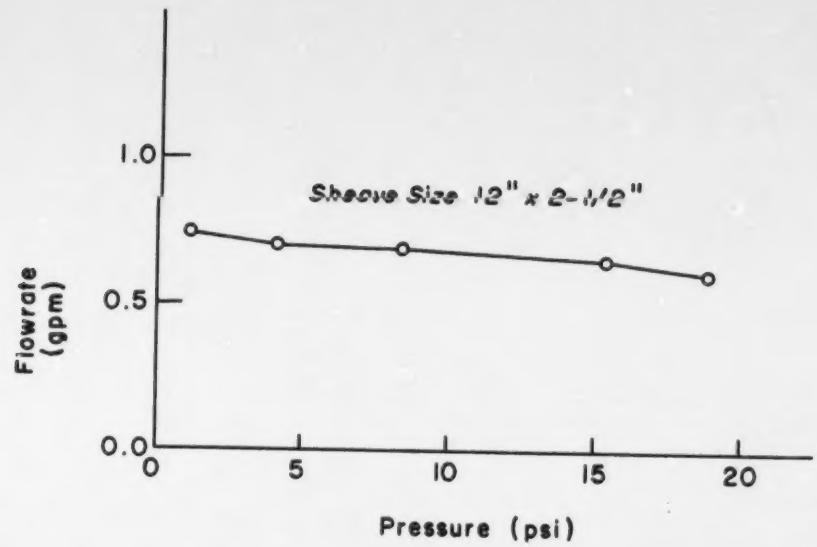


Figure 2. Pressure vs. flow-rate for experimental pilot-plant.



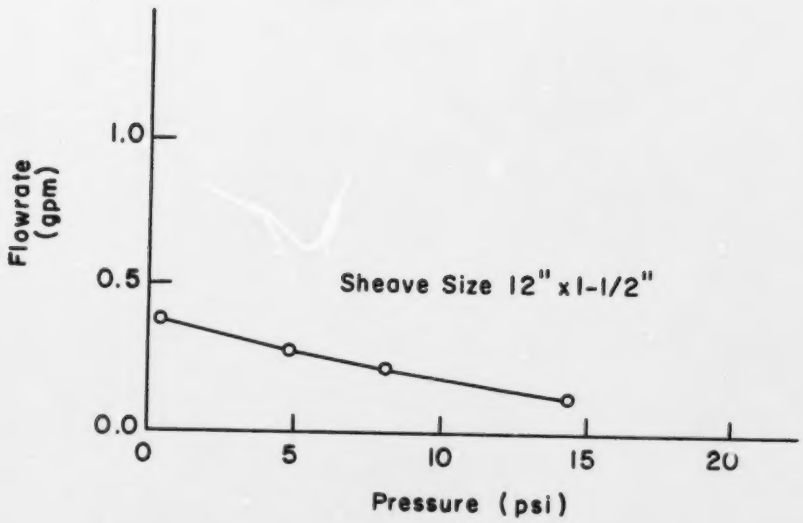


Figure 3. Pressure vs. flow-rate for experimental pilot-plant.

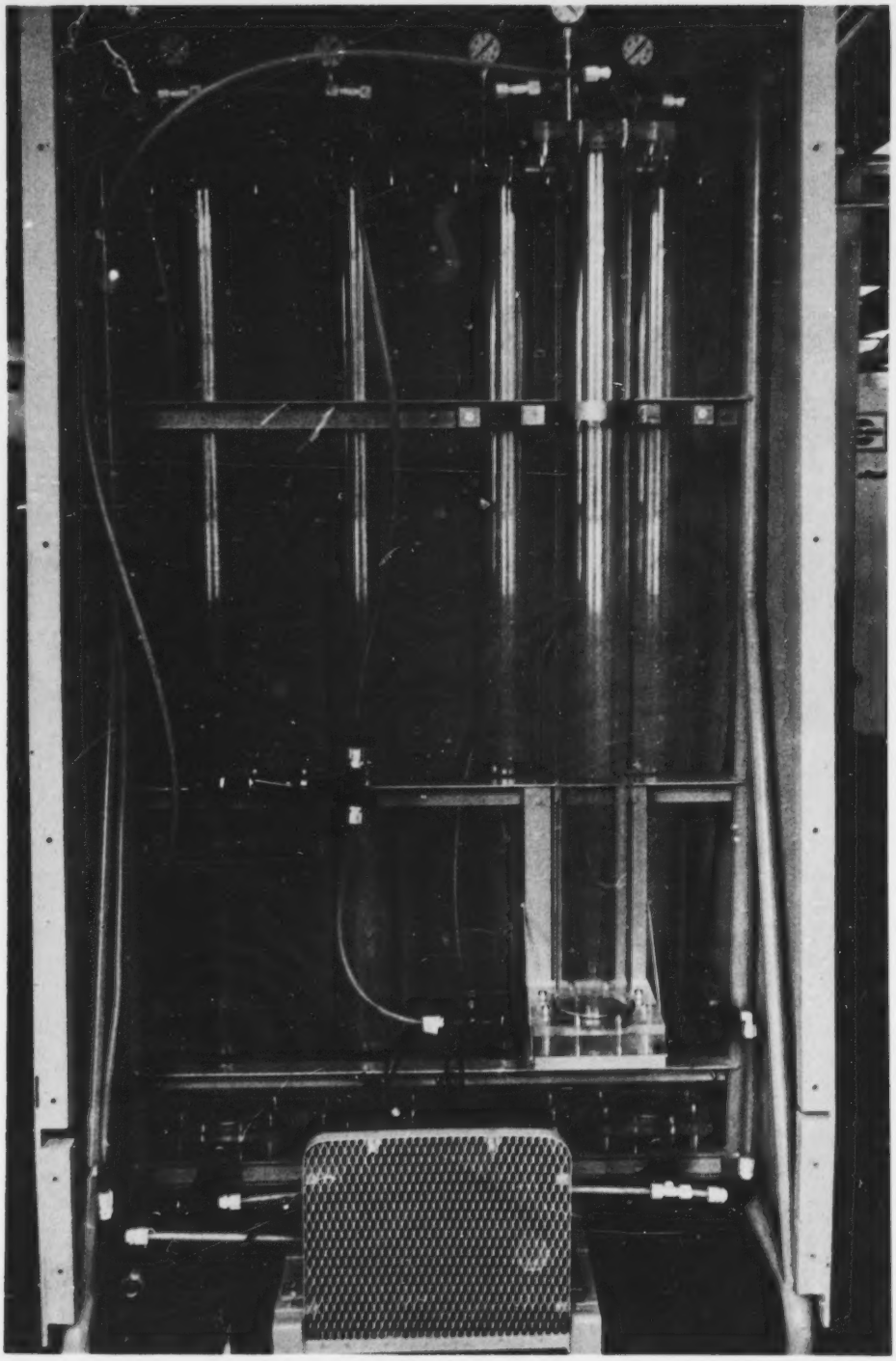


Figure 4. Photograph of completed pilot plant ready for shipment to Gulf South Research Institute, Baton Rouge, Louisiana.

1) Variable speed pump

Pump speed and liquid flow rate are controlled by motor drive and pump pulley sizes. Pulleys supplied with the pump provide flow rates ranging from 0.39 to 0.97 gallons per minute. The tubing provided with this unit is "Viton" tubing.

2) Electric motor

A 110 volt A.C. 1/4 H.P. (explosion proof) totally enclosed motor is provided with the pump.

3) Filter column

4) Adsorption columns

The assembly consists of four 5" I.D. x 72" long "Lucite" plastic columns, in series array, interconnected with 1/2" diameter poly-proprophylene tubing.

5) Temperature and pH monitor

A flow through chamber containing pH and temperature sensors is provided. Flow-through chamber provides opportunity to locate the pH and temperature sensor at any point in the pilot plant. A dual channel "Rustrak" recorder is provided with the instrument.

The activated carbon sorption pilot plant was pre-packaged and delivered in a ready-to-be-used condition. All of the major units such as, pump and drive motor assembly, columns, valves, pressure gauges, and interconnecting tubing, were assembled. The location of the pH-temperature sensor and orientation of flow, i.e., upflow or downflow, were variable and optional. Specific instructions about the pilot plant were enclosed with each unit along with a notice that the packing case was designed and constructed as a reusable shipping container.

Preparation for on-stream operation of activated carbon sorption pilot plant involved the following tasks:

1) selection of flow regime (upflow or downflow) and flow rate, and

2) preparation of carbon sorbent

Instructions for flow rate selection were included along with instructions for valve and tubing connections for upflow and downflow conditions.

Enclosed instruction suggested that activated carbon sorbent is prepared for column application by wetting and soaking. This operation could be accomplished in small batches or completely in one large mixing vessel. It was recommended that the activated carbon mix be permitted to soak for 24 hours prior to charging the columns.

Columns were prepared for application by placing a double layer of fiberglass window screen material (about 1/16 mesh) in the bottom of the column followed by a 4 to 6 inch layer of pea gravel.

Adsorption column preparation is completed by adding the carbon water slurry to the columns. Approximately 3 1/2 feet of carbon is used in each column. In case of very turbid water or water with high solids content it is recommended that the depth of carbon in the first column be reduced to 2 3/4 feet. This condition prevents rapid plugging of the first column.

Each of the adsorption columns was equipped with a pressure gauge. This device is particularly useful when a high turbidity, or high solids, effluent waste stream is being investigated. Under these conditions, it is probable that one column may become partially plugged or saturated with debris. This condition will generally produce a relatively high pressure drop across one of the columns which will be indicated by a high pressure gauge reading.

A Dole flow control valve limits the backwash flow to approximately 4 gpm. This should be sufficient for cleaning the carbon and sand in the five columns. A 30 to 50 percent bed expansion indicating that the backwash flow quantity is sufficient.

Whenever the carbon has been allowed to drain and has been exposed to air for ten minutes or more, it should be backwashed.

Whenever the pressure in Column 1 is 18 psi or more, the columns should be backwashed.

The three way valves have no positive stop, thus, they must have plugs inserted during backwash or they will leak.

SECTION 5

LITERATURE SURVEY

Advanced waste treatment studies, using activated carbon sorption in large scale study, were initiated in 1960. Since then, the application of activated carbon adsorption to the reclamation of waste water has been subjected to continuous investigation. Prior to 1960, activated carbon sorption was considered to be a final clean-up polishing operation following secondary biological treatment. However, by employing this common treatment approach, some investigators (1,2) have reported that leakage difficulties were experienced with the removal of refractory organic materials from the secondary effluent by carbon adsorption process. The nature of organic leakage is thought to be comprised partially of non-adsorbable cell fragments produced during the secondary biological stage and small organic molecules which have been extensively hydrolyzed in the biological treatment system. Because of the leakage problem, Weber et al. (3), attempted a new treatment scheme which consists of conventional primary treatment, chemical coagulation and clarification, filtration, and carbon adsorption. Weber, and his co-workers reported that an exceptional high degree of removal of BOD and suspended solids were achieved using this scheme. Phosphorous and organic nitrogen were removed by chemical coagulation, and nitrates were removed in the carbon adsorber. This process is usually considered to be tertiary treatment and the effluent quality is high, perhaps fit for Human consumption. The advantages of such a process, over the conventional biological processes, are: it is capable of intermittent operation, responds rapidly to shock load variation, easy to operate, amenable to instrumentation and automation, provides removal of high molecular weight biologically resistant substances and toxic

organic waste materials, and requires small space for operation.

The carbon-sorption tertiary treatment has been successfully employed, in large scale operation, in South Lake Tahoe (4). The plant efficiency, in terms of removal values for various components, was: BOD-99.4 percent, COD-96.4 percent, MBAS-99.9 percent, P-99.1 percent, suspended solids, color, coliform bacteria-99 percent, turbidity-99.9 percent. Obviously the quality of the effluent influences cost. This tertiary treatment scheme (5) is reported to cost more than twice the conventional biological treatment. However, it represents an improvement in treatment; it is a step ahead of biological treatment.

Many investigators have experimented with process schemes similar to that of Weber et al., with and without modifications. Cohen and Kugelman (6) designed an almost identical process scheme with packed column carbon adsorber operating at a hydraulic loading of 2 to 8 gpm per square foot and a contact time of 30 to 60 minutes. Their investigations, with municipal waste, revealed that as the contact time increased from 0 to 30 minutes the rate of absorption increased; between 30 and 60 minutes of contact time the rate of adsorption remained almost constant; but higher than 60 minutes contact time resulted in a decreased adsorption rate. The removal of total organic carbon (TOC) and COD were reported as 0.15 to 0.13 pounds and 0.4 to 0.6 pounds, respectively, per pound of activated carbon. They also estimated the cost of treating 1000 gallons of wastewater as 24 to 36¢ for a 6 MGD plant, 18 to 27¢ for a 10 MGD plant, and 9 to 15¢ for a 100 MGD plant.

Shuckrow et al., (7) modified their process scheme for treating municipal waste by incorporating a two stage carbonation process following clarification. The carbonation step is followed by mixed media filtration,

carbon adsorption, and disinfection. The hydraulic loading and superficial detention time, for the carbon column, were 20 gpm per square foot and 30 minutes respectively. They have reported that pH influences the rate of adsorption.

Friedman et al., (8) designed a scheme with a sequence of operation of coagulation, clarification, and carbon adsorption for 75 percent domestic and 25 percent industrial waste. Villiers (9) recommended a series of lime clarifiers, dual media filter, clarifiers, and carbon adsorption to treat municipal waste. Bishop (10) also investigated the application of physiocochemical treatment process, for municipal wastewater, with an automated pilot system consisting of cyclone degritting, two-stage high pH lime precipitation with intermediate recarbonation, dual media filtration, pH control, selective ion-exchange, and downflow granular carbon adsorption. Peoples et al., (11) used a combination of sand filter and activated carbon adsorption for refinery waste and reported the following removal values; suspended solids-62 percent, BOD-85 percent, TOC-65 percent, oil-85 percent, and phenol-99 percent. Huang and Hardie (12) evaluated the use of carbon adsorption process for the treatment of acidic and strongly organic chemical wastes. Using both batch and column techniques, they found that the process could effectively remove COD along with organic nitrogen and turbidity. However, the process did not remove phosphorus, and the pH had no influence on adsorption.

Activated carbon is available for use in two forms, granular and powder. The unit operations and the process characteristics are different for the two forms of carbon, and each has its advantages and disadvantages. The granular carbon has high absorption capacity (depending on application) and can be regenerated by the thermal method, but it is more expensive and requires more sophisticated technology. On the other hand, powdered carbon is much less

expensive than granular form. The small particle size reduces the dependence of adsorption on intraparticular transport and requires a simple unit operation, but regeneration methods are not well developed.

Kropp and Gitchell (13) designed a two stage counter current powdered carbon adsorption scheme with clarifiers after each stage for flocculation and removal of the carbon, followed by sand filtration for the secondary treatment of the domestic waste water. Shell and Burns (14) designed a scheme in which the chemical treatment was followed by powdered carbon adsorption and granular media filtration. The effluent characteristics were reported as; suspended solids-3 mg/l, total phosphorus as P-0.3 mg/l, total organic carbon-12 mg/l, COD-2 mg/l, BOD-10 mg/l, and pH-7.0 to 8.0. The cost was estimated as 18 to 22¢ per 1000 gallons for a 10 MGD plant.

A key to the economic use of the adsorption process is the regenerative capacity of the spent carbon. One theory predicts that in the process of regeneration the kinetic energy of the adsorped impurity is increased to overcome the surface bond energy by subjecting it to a driving force, usually thermal energy. Thermal regeneration is thought to occur in three steps: first, drying at approximately 220°F, followed by pyrolysis of adsorbed molecules at 500-1550°F, and activation at 1600 to 1700°F (15). At such high temperatures the chemical reactivity of the activated carbon is also enhanced and if the atmosphere is not carefully controlled, the carbon itself may be lost due to chemical reaction. The proper control of the atmosphere is critical for effective regeneration. From many experiments the conductive atmosphere to minimize carbon losses are found to be vacuum, nitrogen, and steam. In normal industrial practice, careful operation could minimize carbon losses to 5 to 10 percent of the original quantity. As far as the economics of regeneration are concerned, the

capital and operating cost of regeneration vary substantially with the amount of carbon to be regenerated, type of industry, the spent carbon handling characteristices, method of collection and original carbon activity.

In a laboratory scale experiment, Juhola (15) regenerated spent granular carbon, from a tertiary treatment of wastewater, with flue gas and steam activation. The data indicated that the accumulation of alkaline and iron oxide ash catalyze the oxidation of carbon. Leaching with hydrocholoric acid was found to remove the metallic elements and allow regeneration to proceed with less destruction of carbon. Uraono (16) used a 0 to 10 percent nitrogen atmosphere for the regeneration of spent carbon from a sewage treatment plant. Westvaco Corporation (17) developed and commercialized a method using steam activation for the regeneration of powdered activated carbon. A 5 to 10 ton per day system is estimated to cost $400,000 and $650,000, respectively, and the operating costs are estimated to vary from 2.3 to 5¢ per regenerated pound of carbon, depending on unit size. Kampt (18) used a multiple hearth furnace for thermal regeneration of granular carbon. The first two hearths of the furnace were used for drying, the third and fourth for the pyrolysis of volatile matter, and the last two for the removal of remaining impurities and reactivation, with a total detention time of 30 minutes. The loss of carbon during reactivation averaged 5 to 7 percent. Knopp and Gitchell (13) reported that the composition of carbon gradually changed as it was reused. This was probably due to certain elements of original structure which are preferentially removed by partial oxidation in the regeneration, or to materials which may be deposited from wastewater by precipitation, and subsequent to oxidation, remain as ash. In general, the inorganic content was found to increase. The amount of phosphorus

increased 36 times due mainly to the precipitation of calcium, iron, or aluminum phosphates. The amount of carbon decreased to about 76 percent and the composition of carbon changed from $C_{14.8}\ H_{8.4}O$ to $C_{3.9}\ H_{3.6}O$.

A second method of regeneration is chemical regeneration. Shriba and Purcupile (19) developed a chemical regeneration method called immisible fluid displacement. A solvent, such as carbon disulfide, is contacted with the spent carbon subjecting the adsorbed molecules to a driving force due to their solubility in the solvent. However, the driving force provided by the solubility is far weaker than the temperature gradient in thermal regeneration. Moreover, since the driving force is due to the solubility of the solute in the solvent, desorption can be very selective requiring more than one solvent to treat a waste normally encountered in industry. This method of regeneration can normally be used to recover a particular constituent of the waste. Yet another method of regeneration, primarily of academic interest, is electro-chemical regeneration (20).

Adsorption processes finds wide application in wastewater treatment for many industrial wastes. Azuma (21) treated wastewater from the plating industry to remove chromates and cyanides. Kalinske (22) enhanced the biological oxidation of organic waste in microbial suspension by the addition of activated carbon, for microbial activity. DuPont (23) developed a method in which the addition of powdered carbon to the aerator of a biological treatment resulted in effluent as good as tertiary treatment. The activated carbon adsorption process has been used to treat the wastewater from coke plants (24) and textile plants (25,26). The process has also been applied to oily wastes (27) and radioactive wastes (28).

Utilization of activated carbon for removal of organic waste materials from domestic and industrial wastes is usually provided by sorption columns,

generally the waste stream contacts the carbon column at a predetermined rate in either a downflow or upflow configuration. The contact sorption process is effective in removing waste materials from the waste stream and produces waste saturated carbon or spent activated carbon. In order to restore the sorption capacity of the spent carbon, it is necessary to regenerate the carbon. Methods available for regenerating activated carbon are varied and range from simple displacement reactions to complex high temperature reactivation processes.

Most activated carbon regeneration methods consist of processes directed towards removing the sorbate from the spent carbon. Consequently, practically any process which effectively removes the sorbate, either by removal, per se, or by initiation of a physical or chemical reaction which culminates in removal of sorbate material without disturbing the activated carbon stucture might be an effective regeneration process. Recently, it has been demonstrated that sewage saturated activated carbon can be effectively regenerated by biological oxidation (29, 30).

Inherent in most on-going carbon regeneration methods is the theory that the sorption nature and capacity of activated carbon is an intrinsic property developed by activation which is diminished by the sorbate loading. If this is the case, the specific sorption capacity of activated carbon sorbent is not depleted by utilization, and the original sorption capacity can be reestablished by regeneration. In this context, regeneration and sorption are considered reversible processes.

It is difficult to generalize about the regeneration properties of activated carbon since it is a proprietary material, however, it is generally recognized that high temperature and high pressure treatment, together with selected chemical reagents, are used to achieve activation during

manufacture. Perhaps for this reason, the most popular method of activated carbon regeneration is high temperature treatment. Currently, high temperature regeneration of activated carbon is employed and temperatures ranging from about 200 to 1800°F are used to achieve 95 to 100 percent regeneration (31). The high temperature regeneration process requires either a multiple hearth furnace or rotary kiln equipment. In practice a carrier gas is forced through the carbon waste material during thermal regeneration. The purpose of the carrier gas is two-fold: (1) to provide efficient convective heat transfer to the granular carbon and (2) to protect the carbon and furnace or kiln from burn out. The carrier gas is generally formulated to contain H_2, N_2, H_2O and small amounts of oxygen, and serves as a mild oxidant.

Since the process of thermal regeneration of spent activated carbon is very similar to the process of activation used in preparation of this material, consideration of thermal activation response is appropriate. A comparative study of nine activated carbons, representative of nine different activation processes, showed that the final product exhibited dissimilar specific sorption capacities for methylene blue, phenol, iodine, molasses, and caramel sorbates (31). This finding suggests that the thermal activation process may determine the sorbate-sorbent affinity and the sorption capacity of the activated carbon. This was verified in an additional study wherein a common pine wood char was activated using high temperature air and steam carbonization treatment (31). Results of this study showed that the sorption affinity and capacity of pine wood chars was determined by the activation process.

The role of the activating gas has been identified as a specific mild oxidizing agent. Hassler (31) states "When proper activation conditions are

provided, the oxidizing action of the activating gases does not consist of an indiscriminate removal of successive layers of atoms from the surface". Consequently, oxidation of a sorbent surface probably proceeds as selective errosion of the surface which increases surface area and porsity and generally improves the specific affinity of the sorbent surface.

The most interesting features of thermal activation, relative to this investigation, is the pattern of sorption capacity increase with increase in activation time exposure. Results of two studies (32) show that there is a dissimilar response in sorption capacity increase using malachite green, methylene blue, molasses, and phenol. Malachite green and phenol produced a smooth convex curve, i.e., the sorption capacity increased rapidly at small activation times and then leveled out. Methylene blue exhibited a linear response and sorption capacity increased about 12 percent for each 10 minutes of activation exposure. All of the other sorbate materials, aniline blue and molasses, showed a smooth concave curve type of response wherein the sorption capacity increased rapidly after about 40 minutes of activation exposure. The most interesting result of this study was the convergence of all curves to a common maximum point after about 50 minutes activation exposure.

Unfortunately, the specific experimental conditions used in the above studies were not described, yet it seems probable that the activated time basis was probably developed by limiting the exposure time of a carbon sample. If this were the situation, then the activation time basis is very similar to regeneration time, and/or temperature, used in this study and the opportunity for comparison is provided.

SECTION 6

ACTIVATED CARBON-PETROCHEMICAL WASTE SORPTION

The purpose of this portion of the study was to determine the specific sorption characteristics of four petrochemical liquid wastes and to determine the vacuum thermal regeneration response of the waste carbon combination.

Four petrochemical wastes, provided by Gulf South Research Institute, were used to determine the sorptive capacity of four representative activated carbons. The physical properties of the activated carbons, labeled A, B, C, and D are presented in Table 2.

The petrochemical wastewater analyses, labeled I, II, III, and IV are representative of typical petrochemical industries. The chemical components for each waste were different depending on the products and processes of the industry. Efforts were not made to identify each component present nor to analyze quantitatively for specific products. The information provided about the waste characteristics is listed below.

Waste I

The composition of Waste I is as follows:

Methyl chloride	2 ppm
Chloroform	683 ppm
Ethylene-di-chloride	8331 ppm
COD	16100 ppm
Chloride as Cl	7960 ppm
Alkalinity	0.0
pH	<0.1

Waste II

The components of this waste are naphthyl and similar ring structured compounds together with unsaturated hydrocarbons. Other components were:

COD	106680 ppm
TOC	1810 ppm

TABLE 2

PHYSICAL PROPERTIES OF ACTIVATED CARBON USED IN STUDY

Carbon	A	B	C	D
Manufactorer	Westvaco Chem Corp.	Witco Chem Corp.	Am. Norit Corp.	Calgon Corp.
Trade Mark	Nuchar	Witco	Norit	Filtra-sorb
Mesh Size	12 x 40	12 x 30	8 x 20	
Surface Area m^2/g	850	1050		1100
App. Density g/cc		0.48		0.44
Real Density g/cc				2.1
Part Density	1.4	0.92		1.35
Effective Size	0.65			0.60
Uniform Coeff.	1.60			$\leq$1.9
Pore Volume		0.6		0.94
Iodine No.	850			1000
Ash %	7	0.5		8.5
Moisture Max %	2			2

Alkalinity	1475 ppm as $CaCO_3$
Chloride as Cl	14 ppm
pH	9.7

Waste III

This waste contained chlorinated methyl group hydrocarbons. Other known details were:

pH approximately	2.0

Waste IV

The essential components were:

Methyl Chloride	0-40 ppm
Ethyl Chloride	0-30 ppm
Ethylene/dichloride	9122 ppm
COD	1764 ppm
Alkalinity	1369 ppm as $CaCO_3$
Chloride as Cl	2662 ppm
pH	11.0

Total organic carbon was used as the waste concentration parameter. Since some of the waste materials were highly volatile, the actual procedure of acidifying the sample and purging with nitrogen gas, for measuring organic carbon, would have resulted in substantial organic loss from solution. In the carbon analyzer, the instrument used for the quantitative analysis of total carbon, the sample was carried by oxygen gas through a furnace at 960°F. At this temperature the organic and inorganic carbon compounds present in the sample would be decomposed to carbon dioxide and water in the furnace. The water formed in the process is trapped in the manometer and carbon dioxide is carried through an infrared analyzer. The response proportional to the carbon dioxide present is transmitted to the recorder. The concentration corresponding to the response was obtained from a standard curve. It should be indicated that by this method of analysis of the waste, before and after the carbon adsorption treatment, the extent of removal of total organic carbon was obtained.

It was not possible to identify the particular component that was removed. The carbon composition of the wastes is presented in Table 3.

The removal of organic carbon from the wastes is more important for analysis of carbon adsorption efficiency than the total carbon. However, it is possible to estimate the inorganic carbon in each waste from the general characteristics of the wastes. Wastes I and III have a pH of <0.1 and 2.0, respectively, under this condition no inorganic carbon remains in solution. Therefore, for Wastes I and III the total carbon is equal to organic carbon. For Wastes II and IV the estimation was made from the results of column study by making the assumption that the initial leakage was purely inorganic carbon, which was 55 mg/L and 80 mg/L for Waste II and IV respectively. The inorganic portion of total carbon was also estimated from the pH and alkalinity data provided by Gulf South Research Institute as 300 Mg/L and 182 mg/L, respectively. As the results of the isotherm study support the values obtained from the column study, the values obtained from pH and alkalinity were ignored.

Isotherm Study

The isotherm study is a laboratory simulation of a batch process in which the activated carbon is contacted with the waste under continuous stirring and constant temperature until the adsorption reaches equilibrium. The batch isotherm results are a true measure of sorption affinity, as there is no other physical process contributing to the removal of solutes.

The Warburg apparatus was used for this study because it offered temperature control and continuous mixing. The extent of adsorption of solute onto activated carbon is a measure of the equilibrium in the adsorption process. At a constant temperature it is a function of the concentration of solute in the bulk solution. The functional expression of the distribution

TABLE 3

RESULTS OF ANALYSIS OF RAW WASTE
FOR ORGANIC AND TOTAL CARBON

Waste	Total Carbon	Inorganic Carbon	Organic Carbon
I	4368 ± 288	0	4368 ± 288
II	2885 ± 365	55	2830 ± 365
III	43 ± 7	0	43 ± 7
IV	350 ± 6	80	350 ± 6

ratio and the solute concentration in the bulk solution is called the adsorption isotherm. The distribution, expressed as the amount of solute adsorbed per unit mass of activated carbon, is a function of the concentration of solute remaining in solution at equilibrium. This is not only a convenient form for representing experimental data, but also a useful starting point for the development of theoretical treatment of adsorption equilibria. Theoretical and empirical models have been developed to represent the experimental data. These models are discussed below.

Langmuir Model

This model can be deduced from either kinetic considerations or from the thermodynamics of adsorption with three principal assumptions: 1) maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, 2) the energy of adsorption is constant and, 3) there is no transmigratory activity of adsorbate molecule in the adsorption surface. If an adsorption process satisfies these conditions, it will follow

$$\frac{C}{X/M} = \frac{1}{b\,X_m} + \frac{C}{X_m} \qquad (1)$$

where C is solute concentration

X/M is quantity of adsorbent per unit mass adsorbent

X_m is the adsorbate per unit mass adsorbent

b is the energy of adsorption

BET Model

This model could also be deduced from either kinetic considerations or from the thermodynamics of adsorption; but unlike the Langmuir model, adsorption is not restricted to a monolayer. This model assumes that a number of

layers of adsorbate molecules form at the surface and the Langmuir equation applies to each layer. A further assumption of BET model is that a given layer need not complete formation prior to the initiation of subsequent layers. The equilibrium conditions will, therefore, involve several types of surfaces in the sense of number of layers of molecules on each surface site. This model could also be applied to those cases where adsorption takes place at preferential sites. In a mathematical form, this model could be represented as

$$\frac{C}{(C_S - C)\ X/M} = \frac{1}{EX_m} + \frac{E-1}{EX_m}\frac{C}{C_s} \qquad (2)$$

where E is the constant of energy of interaction with the surface

C_s is the saturation concentration of the solute.

Freundlich Model

This model is a special case for heterogeneous surface energies in which the energy term varies as a function of surface coverage due to variations in the heat of adsorption. The equation has the general form

$$X/M = E\ C^{\frac{1}{n}} \qquad (3)$$

and the data fitted to the logarithric form as

$$\log X/M = \log E + \frac{1}{n} \log C \qquad (4)$$

The intercept is roughly an indicator of sorption capacity and the slope, the adsorption intensity.

Column Study

The column study was designed to analyze the dynamics of the adsorption

process under a constant flow of the waste through the void space of a fixed bed of activated carbon. Column operations have a distinct advantage over batch operations because rates of adsorption depends on the concentration of solute in solution and, for column operation, the column is in continuous contact with fresh solution. Whereas, in the isotherm study, no attempt was made to study the effect of transport mechanism on adsorption. The column study is particularly designed to evaluate the transient characteristics of adsorption.

As the waste moves down by gravity through the voids of the carbon bed, the organic carbon is adsorbed rapidly by the upper layer of fresh carbon, the primary adsorption zone, because this layer is in contact with the solution at the highest concentration. The small amount of organic carbon escaping adsorption in this layer is removed in the lower strata of the bed and, initially, no impurity escapes from the adsorber. As the process continues, the top layers of the carbon become partially saturated and become less effective for further adsorption; then the primary adsorption zone moves through the column to regions of fresher adsorbent. As the primary zone moves down, more and more solute tends to escape in the effluent. The breakthrough occurs when there is the appearance of an adsorbate of interest in the carbon bed effluent at a predetermined concentration.

The breakthrough curve, for a column operation, is obtained by plotting concentration against volume of flow. For most operations in wastewater treatment, the breakthrough curve exhibits a characteristic "$\int$" shape, but with varying degree of steepness and position of break point. The factor influencing the break through curve are the flow rate, bed depth, detention time, and all other factors influencing the process of adsorption. The break point is chosen at some low value and exhaustion point is chosen close to the initial concentration of the waste. When the effluent concentration reaches or passes

the break point value and reaches an arbitrary allowable value, the operation should be discontinued and the bed regenerated for further use.

In this study, a 50 ml burette packed with 0.25 to 4.0 grams of activated carbon was used for the packed column and the flow was adjusted to a few drops per minute to maintain a contact time almost equal to that of a conventional pilot plant study. Such a simple experimental set up was resorted to due to paucity of resources. Although the quantitative nature of the results are not identical to those of pilot or scale up processes, it is believed that the results at least describe the nature of the transport mechanism qualitatively.

Regeneration Study

For the regeneration study, Carbon B was chosen as it exhibited slightly superior adsorption characteristics to the other carbons. The choice of waste depended not only on the adsorption characteristics but also on availability. Waste I was not available in the required quantity. Waste II, although not available in its original strength, was available in diluted form after being used for the isotherm study. As the chemical nature of the waste may change when it is subjected to adsorption, Waste II may have a different composition from the original waste. Therefore, it is labeled as waste II-A, since it is believed that the original properties were not changed drastically. Waste III exhibited very poor adsorption characteristics, so it was not considered for regeneration study. Waste IV was available in sufficient quantity and was employed in conjunction with Carbon B and Wastes II-A and IV.

About three grams of carbon was contacted with a large volume of waste until the steady state concentration was reached. The saturated carbon was divided into five parts and each part was regenerated at temperatures in the

range of 0 to 1000°F. Then, an adsorption isotherm was obtained using 10 ml of the waste and varying amounts of carbon - using the regenerated carbon to study the effect of temperature on regeneration.

The spent carbon was regenerated in a high temperature furnace using a vacuum of 50 mm of mercury. The spent carbon was transferred to a boat and inserted into the furnace. After checking for air tightness, the vacuum pump was switched "on" and the vacuum was allowed to build up before switching the furnace "on". As the furnace was heated, the emf generated in the thermocouple was transmitted to the strip chart recorder. The heating unit was turned off when the chart recorded an emf equivalent to the temperature of regeneration since the control system was not designed to maintain a constant temperature. Then the furnace was allowed to cool to ambient temperature under vacuum conditions.

Results and Discussion

The results of the isotherm study are presented in Table 4 for four carbons and four wastes. The first column indicates the quantity of activated carbon M, in milligrams per liter, in a 25 ml sample. The waste may contain volatile matter that escapes from solution when subjected to agitation so, in order to estimate only that portion available for adsorption, the first sample, or reference sample, was run without activated carbon in the flask. The initial concentration of the waste was assumed to be the equilibrium concentration of the reference sample, and the removal of organic carbon, for any other sample was obtained by subtracting the equilibrium concentration of the sample and it is expressed as milligrams per liter. The ratio of X/M was obtained as a dimensionless number and was the mass of organic carbon adsorbed per unit mass of activated carbon.

The characteristics of adsoption isotherms, proposed by Weber (29) are

TABLE 4

RESULTS OF ISOTHERM STUDY

	Carbon A				Carbon B				Carbon C				Carbon D			
Waste	Act. Car. M mg/L	Eqm. Conc. mg/L	Removal x mg/L	X = x/M	M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X
I	0	4080	0	-	0	4656	0	-					0	4656	0	-
	60	3888	192	3.2	60	4512	144	2.4					35	4200	456	13.04
	200	3792	288	1.44	200	4320	336	1.63					175	3620	1036	5.92
	500	3528	552	1.10	500	4164	492	0.98					515	3488	1168	2.27
	1000	3720	360	0.36	1000	3792	864	0.85					900	3060	1596	1.63
	2000	3720	360	0.15	2000	3276	1380	0.69					2015	3060	1596	0.79
					5024	2760	1896	0.38								
					10016	2360	2296	0.23								
					25048	2090	2566	0.10								
					49888	1120	3536	0.07								
II	0	3185	0	-	0	3205	0	-	0	2465	-	-	0	2465	-	-
	644	2885	300	0.466	700	3355	-	-	1896	1985	480	0.253	2292	1373	1092	0.477
	1092	2645	540	0.498	1150	2845	360	0.313	7000	1047	1418	0.202	4000	905	1560	0.390
	5035	1445	1740	0.346	5000	1725	1480	0.296	9088	749	1716	0.187	6000	578	1887	0.315
	10030	197	2988	0.296	10080	725	2480	0.246	12116	421	2044	0.168	8005	353	2112	0.264
	15025	0	3185	0.212	15040	145	3060	0.203	17048	115	2350	0.138	11068	105	2360	0.215
	25100	0	3185	0.127	25100	145	3060	0.122	20136	53	2412	0.120	12808	35	2430	0.191
									23120	53	2412	0.104	14080	35	2430	0.173

TABLE 4 (CONT'D)

RESULTS OF ISOTHERM STUDY

	Carbon A				Carbon B				Carbon C				Carbon D			
Waste	M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X
III	0	50.0	-	-	0	50.0	-	-	0	36.0	-	-	0	36.0	-	-
	95	29.2	20.8	0.217	68	28.0	22.0	0.324	68	32.4	3.6	0.053	100	28.8	7.2	0.072
	204	27.6	22.4	0.110	192	21.2	28.8	0.150	176	30.0	6.0	0.034	216	27.2	8.8	0.041
	348	21.2	28.8	0.083	320	18.0	32.0	0.100	360	27.6	8.4	0.023	308	27.0	9.0	0.029
	420	27.0	28.8	0.066	448	18.4	31.6	0.071	436	27.2	8.8	0.020	404	27.6	8.4	0.021
	584	18.4	31.6	0.054	608	17.2	32.8	0.054	620	28.8	7.2	0.011	636	26.3	9.7	0.015
	840	15.6	34.4	0.041	840	15.2	34.8	0.042	856	26.8	9.2	0.011	844	23.6	12.4	0.015
	1028	15.6	34.4	0.035	1024	15.2	34.8	0.034	1032	27.6	8.4	0.008	980	24.4	11.6	0.012
IV	0	264	-	-	0	264	-	-	0	277	-	-	0	277	-	-
	1992	189	75	0.038	2024	189	75	0.037	2084	234	43	0.021	2092	213	64	0.031
	4004	149	115	0.029	4152	159	105	0.025	3944	202	75	0.019	3948	188	89	0.022
	5188	134	130	0.025	5228	134	129	0.024	5152	196	81	0.016	5012	179	98	0.020
	6040	117	147	0.024	6000	132	132	0.022	5992	185	92	0.015	6008	166	111	0.018
	7116	108	155	0.022	7112	130	134	0.019	7132	182	95	0.013	6928	164	113	0.016
	8000	104	160	0.020	7944	117	147	0.018	8044	176	101	0.012	8298	160	117	0.014

presented in Figure 5. Curves 1 and 3 indicate the curvilinear dependence of favorable and unfavorable adsorption pattern, respectively, and curve 2 represents a combination of adsorption and absorption which occur in direct proportion to concentration. Using this general criteria, the experimental data was analyzed and the results presented in Table 5.

The pattern of favorable and unfavorable adsorption appears to depend on the components of each waste and their respective adsorbability. The recent study of Giusti et al., (33) has established that the amenability of typical organic compounds to activated carbon adsorption from pure component systems increases with increasing molecular weight and decreasing polarity, solubility, and branching. Although multicomponent systems, as encountered in petrochemical waste, have not been studied to the extent necessary, it is probably reasonable to assume that, as the average molecular weight of the components of a multicomponent system increases, the process of adsorption becomes more favorable provided polarity, solubility, and branching do not affect adsorption significantly. As Waste II is composed of components of higher molecular weight, such as anthryl and naphthyl ring structured compounds (34), a favorable adsorption pattern is obtained. It appears that short chain organic chlorides, principal components of Wastes I and IV are particularly resistant to carbon adsorption. This may be because chloride compounds are lyophylic and the intermolecular forces are better balanced when adsorbed. Waste III, on the other hand, composed of methyl group hydrocarbons, exhibited poor adsorption characteristics possibly due to the low average molecular weight of the components. The relative adsorption characteristics of Wastes I, II, III, and IV, with Carbon B, are presented in Figure 6.

The process of adsorption also depends on the nature of the carbon. In

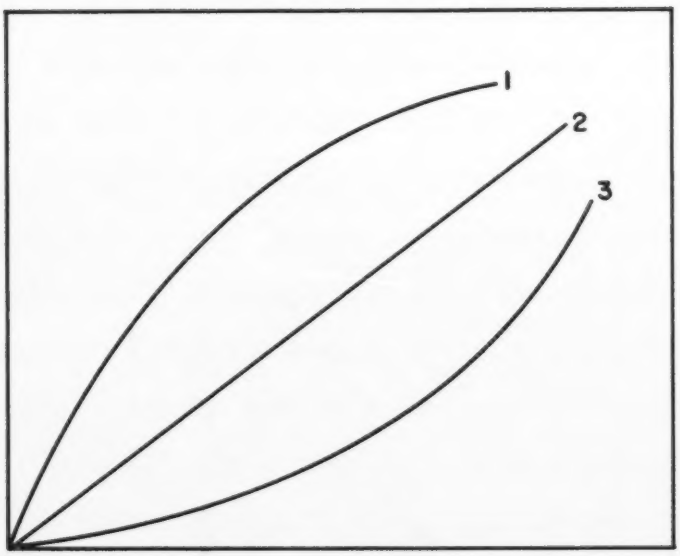


Figure 5. Types of sorption separations after Weber (29): 1. Favorable adsorption; 2. Linear adsorption and adsorption; 3. Unfavorable adsorption.

TABLE 5

SORPTION CHARACTERISTICS OF WASTES STUDIED

Carbon	A	B	C	D
Waste				
I	x	x	-	x
II	+	+	+	+
III	x	x	x	x
IV	x	x	x	x

+ favorable adsorption

x unfavorable adsorption

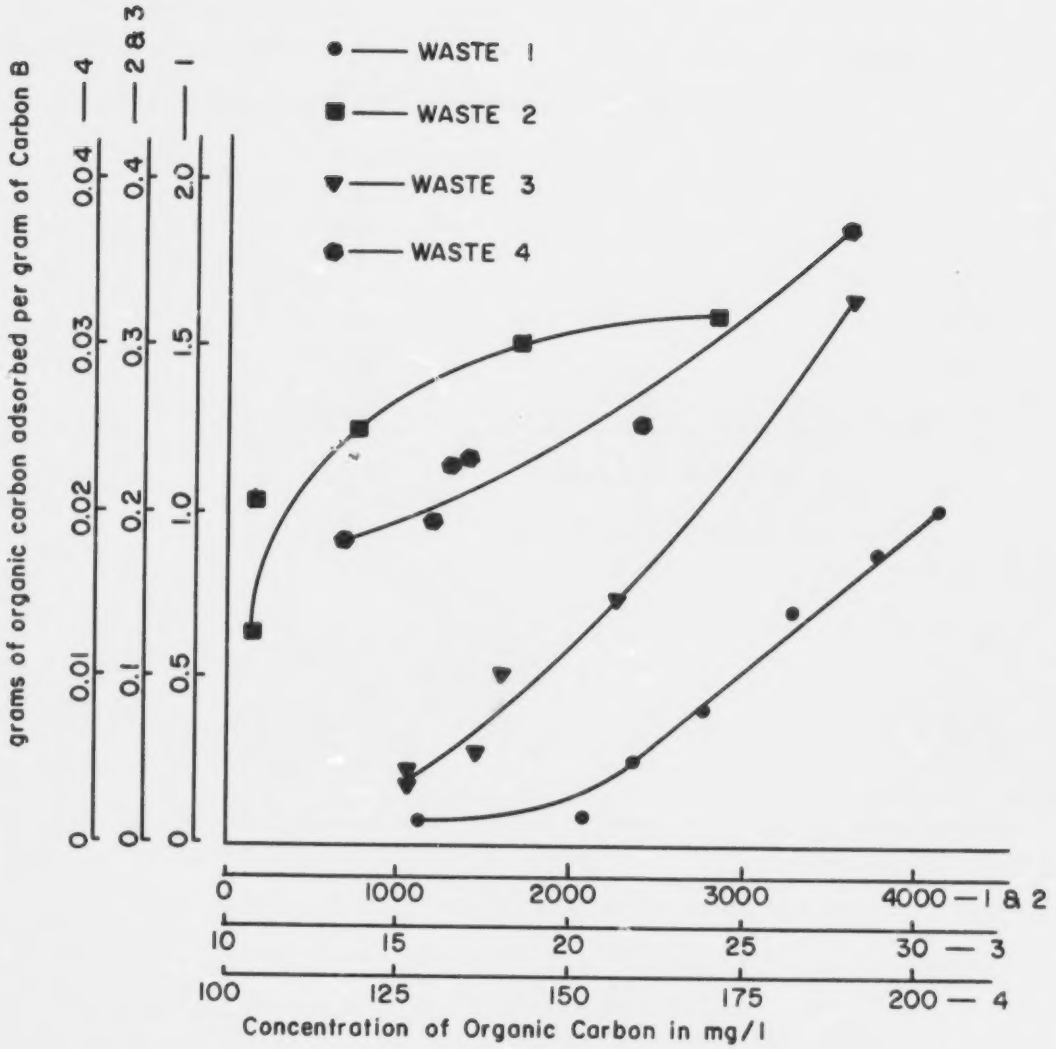


Figure 6. The influence of the source of petrochemical waste on adsorption characteristics: Adsorption Isotherm for Wastes I, II, III, and IV using Carbon B.

Figure 7, the isotherm for Waste II, with all four carbons is presented. Carbon C exhibited by far the poorest adsorption characteristics followed by Carbon B. At concentrations above 400 mg/L of the waste, Carbon D exhibited the best adsorption pattern and below 400 mg/L Carbon A was best. It is important to note that the suitability of a particular carbon depends also upon the range of waste concentration. This phenomenon was noted even for wastes with an unfavorable adsorption pattern. In the case of Waste I, Figure 8, Carbon D was best suited in the concentration range higher than 3000 mg/L, but below this concentration it loses its superiority to Carbon B. However, for Wastes III and IV, Figures 9 and 10 show that Carbons B and A, respectively, were found to give the best pattern over the entire range of waste concentration. Although it was impossible to pick out a carbon that was capable of providing the best pattern for all wastes, the one that exhibited the poorest pattern in all cases was Carbon C.

The results of the experiments do not necessarily have to conform to any of the isotherm models discussed earlier. However, analysis based on these models hopefully will show that one of the models describes the nature of adsorption both quantitatively and qualitatively. The experimental points were fitted to the linearized form of the three models, equations (1), (2), and (4), and it was found that the Freundlich model more accurately described the process than the others. In Figures 8 through 11, the linearized forms of the Freundlich model are presented for all wastes and carbons. The Langmuir and BET models were not as applicable since the linearized form usually resulted in a curve, whereas the Freundlich model always produced a linear response. The lack of fit of the Langmuir and BET models may be attributed to the limitations of the theoretical assumptions used in deriving Langmuir and BET isotherms, or that factors not considered in these two models influence and alter the adsorption pattern. In Figures 12, 13 and 14, the

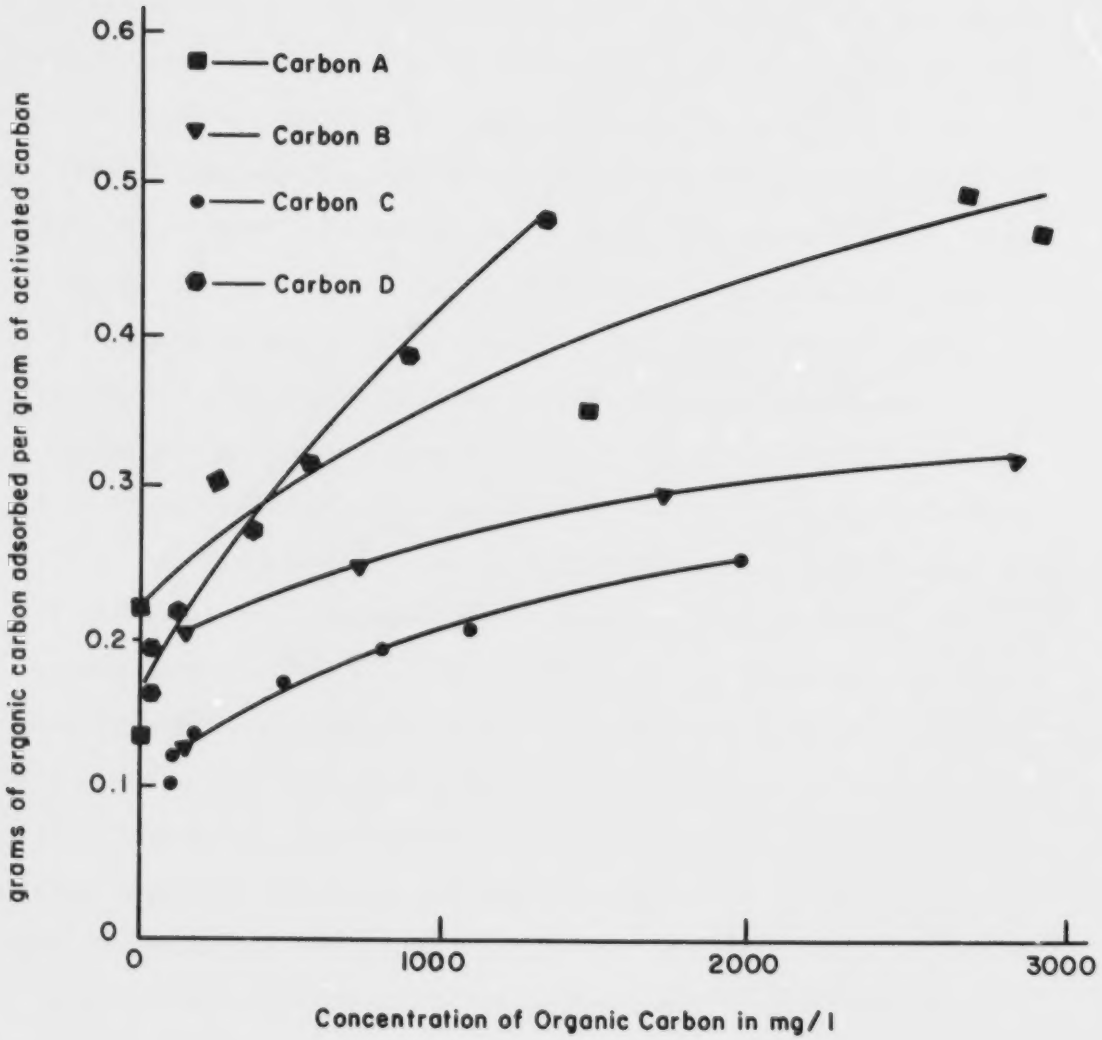


Figure 7. The influence of the nature of activated carbon on adsorption characteristics; Adsorption Isotherm for for Waste II with Carbons A, B, C and D.

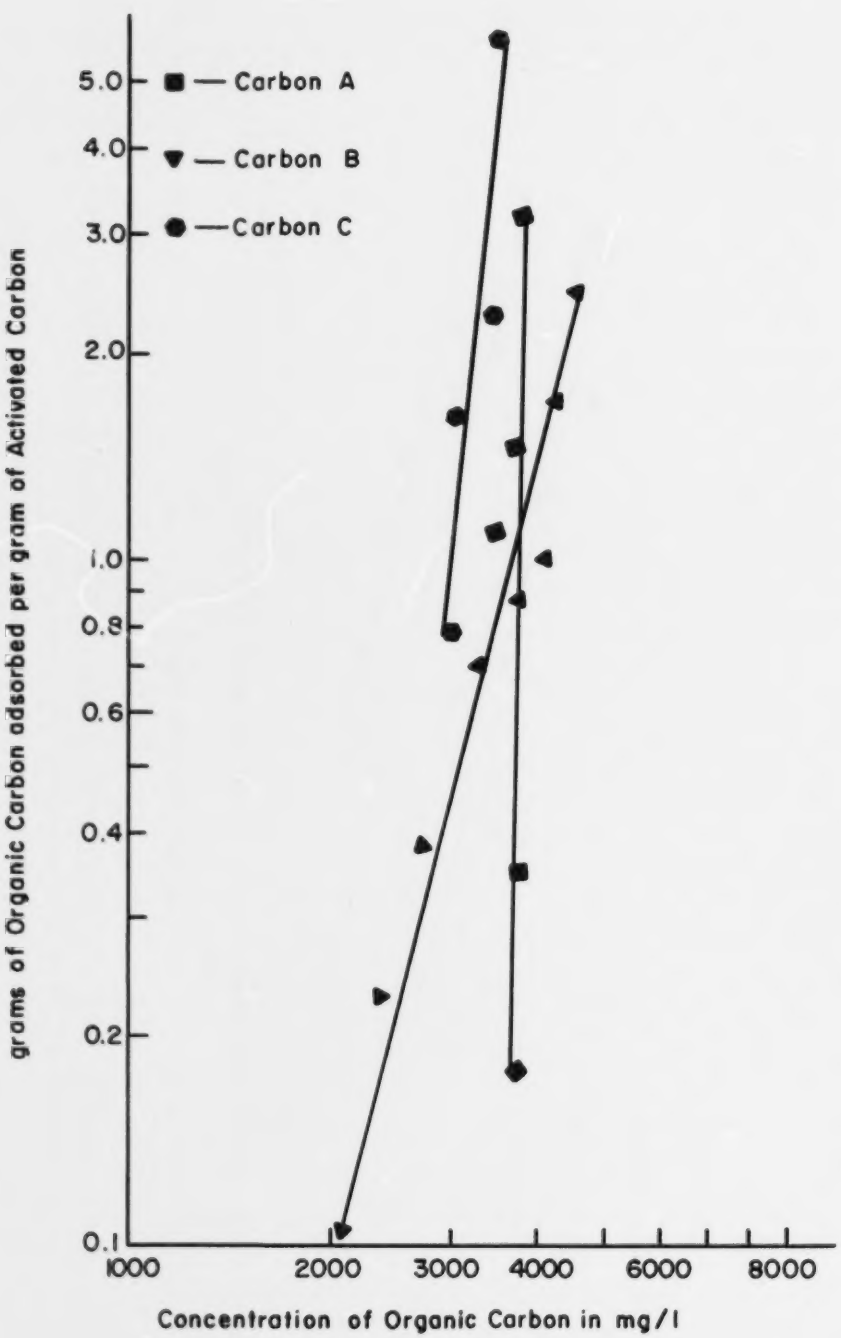


Figure 8. Results of Isotherm Study for Waste I and Carbons A, B and D in the linearized form of Freundlich Isotherm Model.

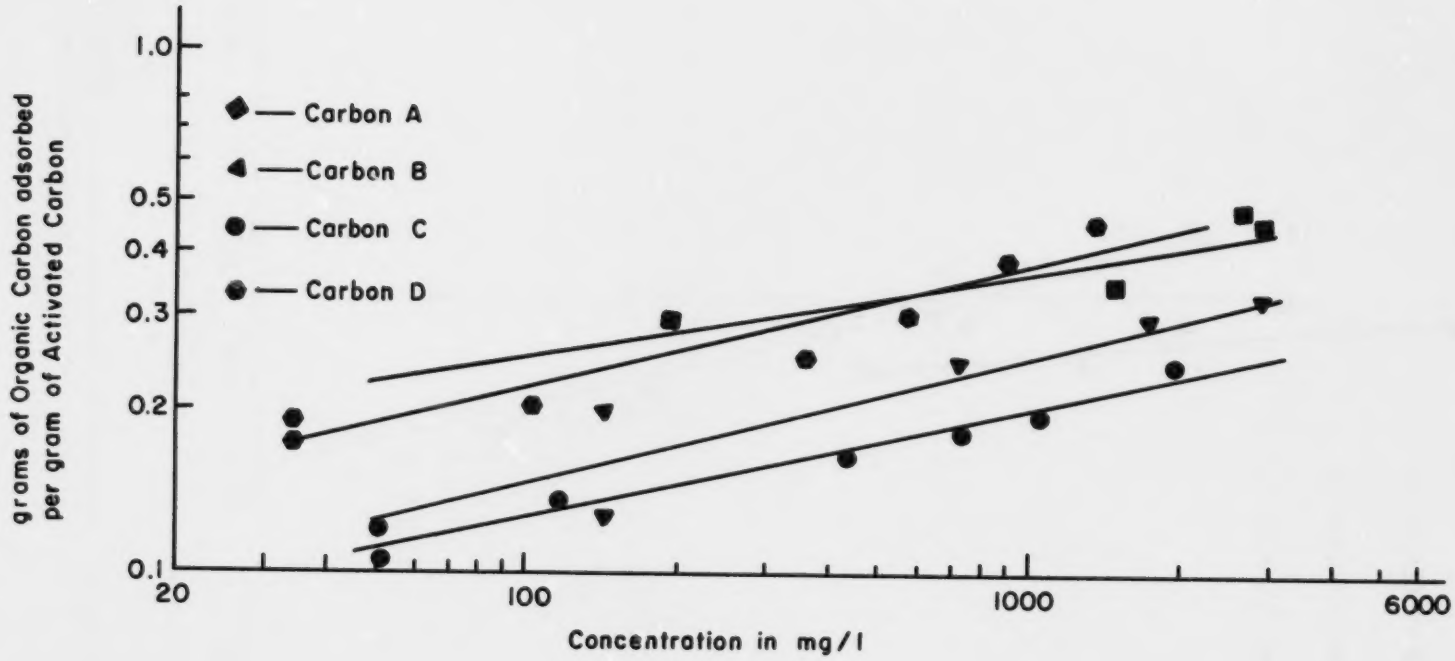


Figure 9. Results of Isotherm Study for Waste II and Carbons A, B, C and D in the linearized form of Freundlich Isotherm Model.

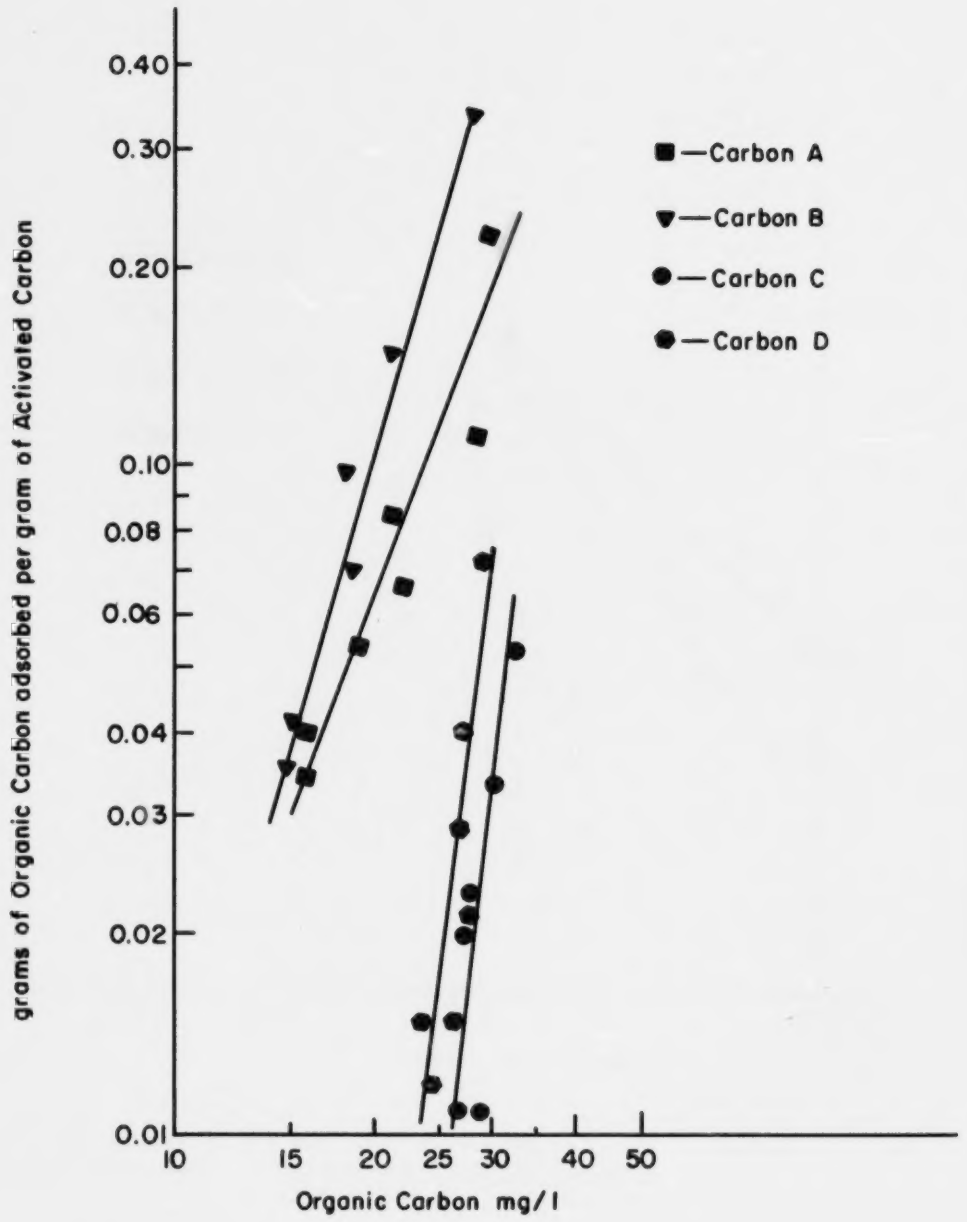


Figure 10. Results of Isotherm Study for Waste III and Carbons A, B, C and D in the linearized form of Freundlich Isotherm Model.

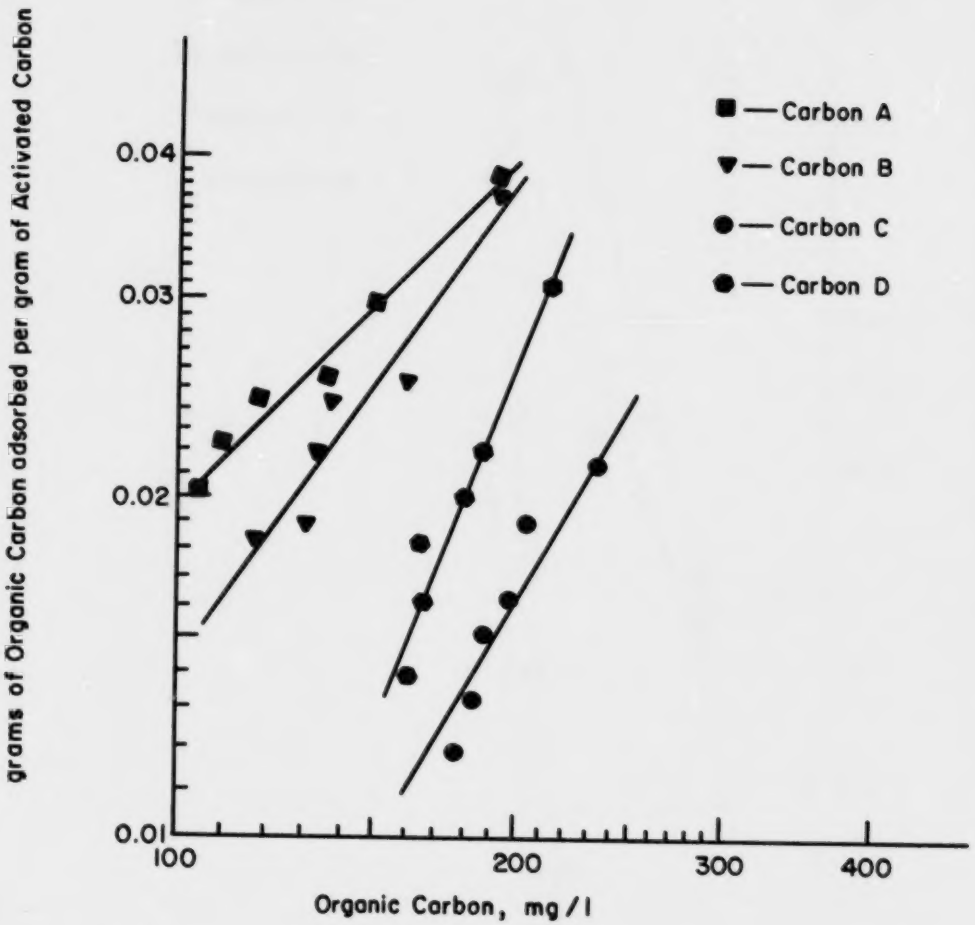


Figure 11. Results of Isotherm Study for Waste IV and Carbons A, B, C and D in the linearized form Freundlich Isotherm Model.

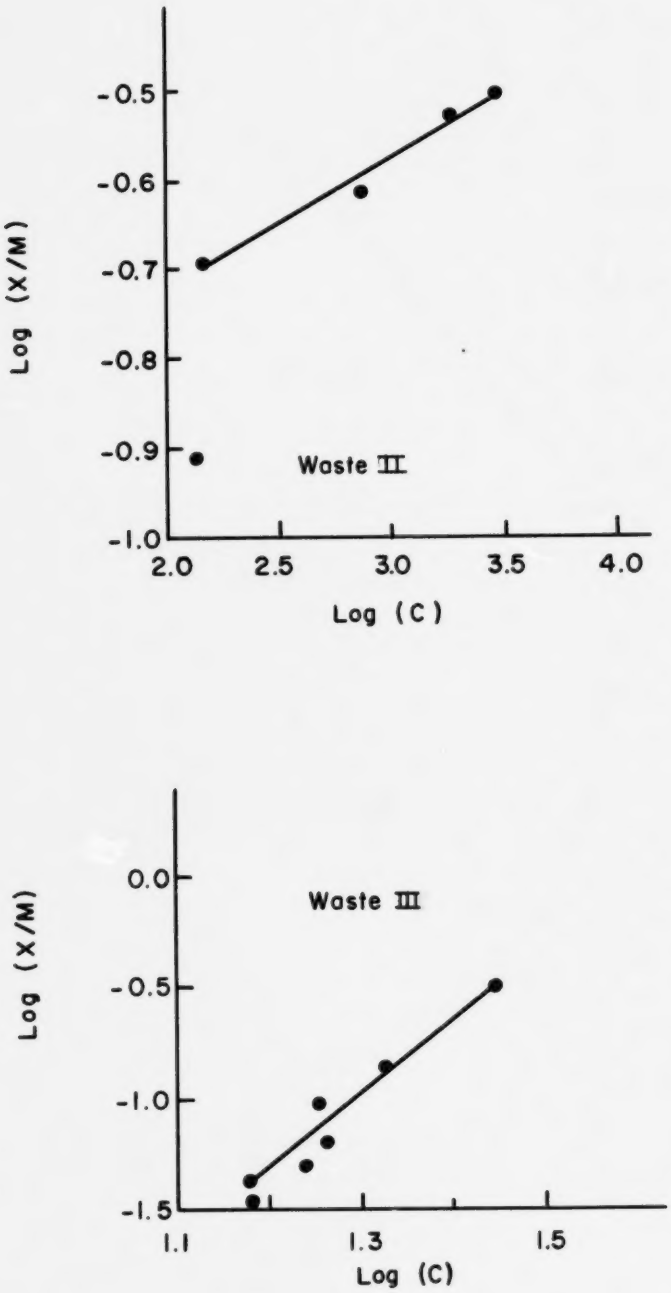


Figure 12. Linearized form of Freundlich Isotherm Model for wastes exhibiting favorable adsorption, Waste II and unfavorable adsorption, Waste III with Carbon B.

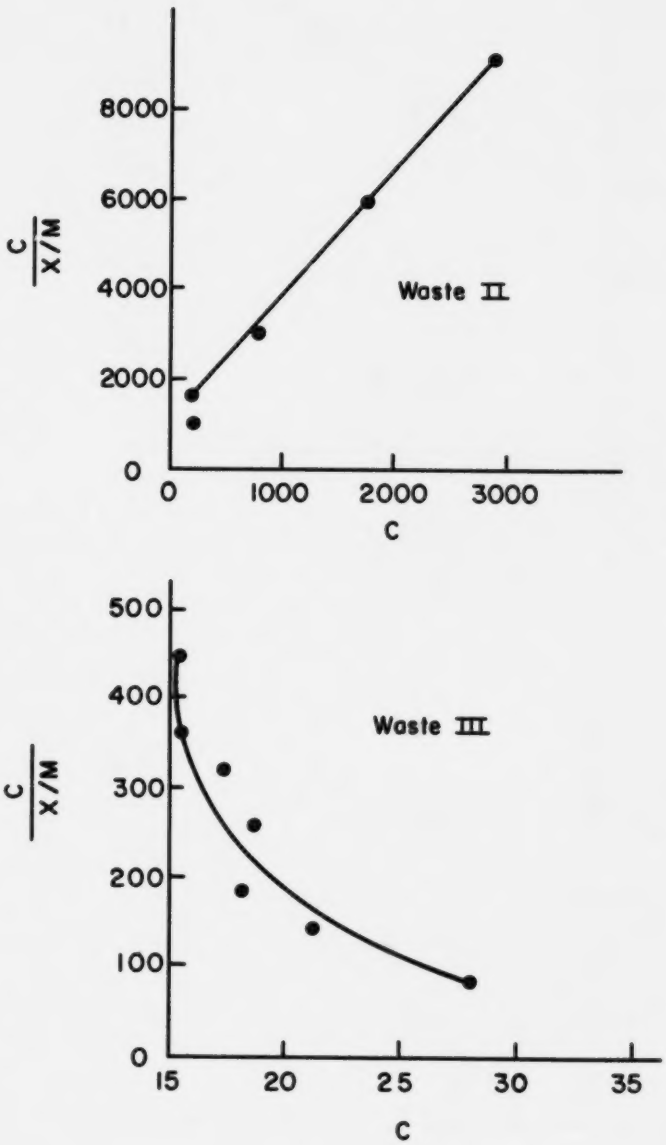


Figure 13. Linearized form of Langmuir Isotherm Model for wastes exhibiting favorable adsorption, Waste II and unfavorable adsorption, Waste III with Carbon B.

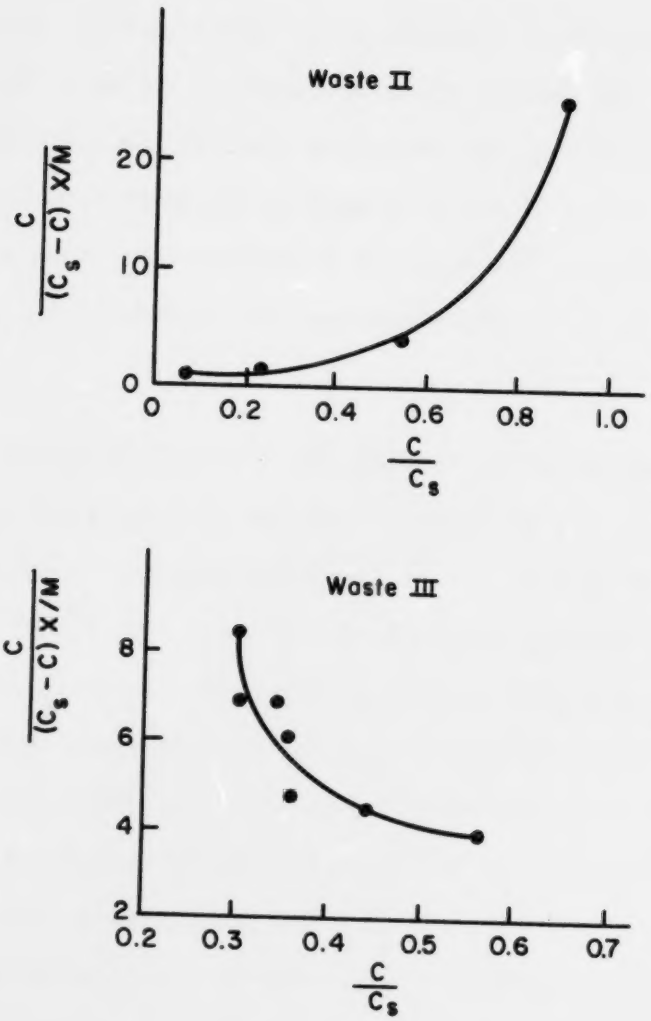


Figure 14. Linearized form of BET Isotherm Model for wastes exhibiting favorable adsorption, Waste II and unfavorable adsorption, Waste III with Carbon B.

three models are presented for wastes which exhibit favorable and unfavorable adsorption, Wastes II and III, respectively, with Carbon B.

In summary, not all petrochemical wastes are amenable to carbon adsorption. Wastes with short chain compounds do not always exhibit favorable adsorption pattern. As the average molecular weight of the waste increases the better the adsorption pattern. No one carbon exhibited the best adsorption for all wastes. The choice of carbon depends on the waste as well as the waste concentration ranges. The empirical Freundlich model more accurately represents petrochemical waste adorption than the Langmuir or BET models.

Packed Column Study

The results of packed column studies, for Waste II and Carbon A, are presented in Figure 15. It was expected that the effluent would approach the initial concentration when the bed reached saturation. However, the initial concentration was not reached by the effluent even though over two liters of the waste was treated. It is believed that the difference between the initial concentration and breakthrough concentrations was caused by some kind of filtration effect. The overall adsorption resulted in the removal of 0.286 grams of organic carbon per gram of activated carbon and adsorption alone contributed to the removal of 0.235 gm/gm concentration and breakthrough concentrations were caused by some kind of filtration effect. The overall adsorption resulted in the removal of 0.286 grams of organic carbon per gram of activated carbon and adsorption alone contributed to the removal of 0.235 gm/gm.

The results of the packed column study, for Waste III and Carbon A indicated a wide scattering of experimental data points. This was attributed to poor adsorbability of the waste - further complicated by inaccuracy in the measurement of total carbon in such low concentration.

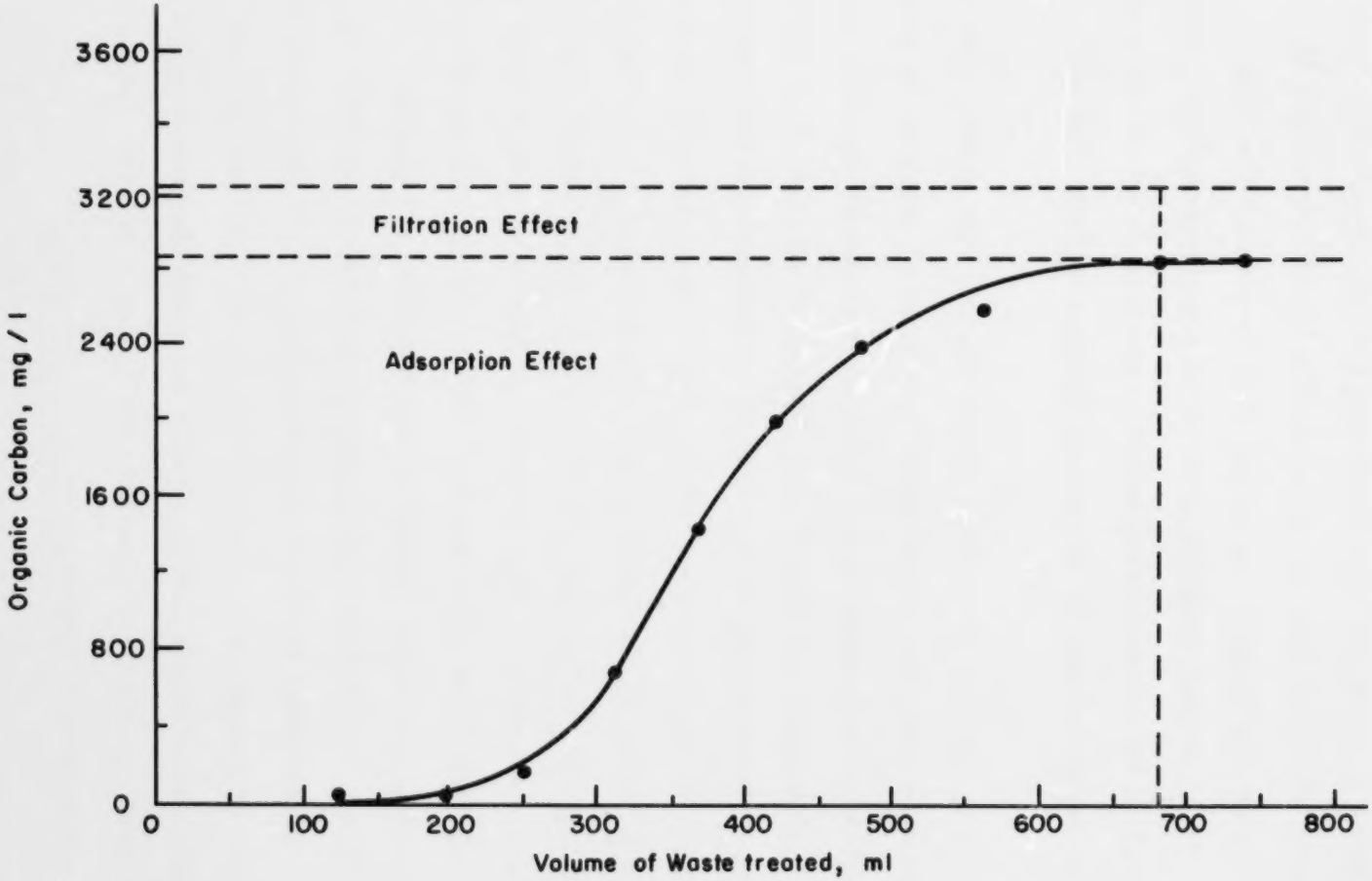


Figure 15. Results of packed column study for Waste II and Carbon A.

In Figure 16, the results of one of the three-column studies for Waste IV and Carbon A is presented. All three have similar breakthrough curves but are vastly different from the characteristic shape observed for Waste II. This may be attributed to the nature of adsorption as presented in Figure 6. The waste that exhibited a favorable adsorption isotherm, Waste II, also yielded the characteristic breakthrough curve in the column study, whereas, the waste that had an unfavorable isotherm deviated from this pattern.

In Table 6, the results of three column studies, with Waste IV and Carbon A, are summarized. The comparison of X/M values of isotherm and column studies, Tables 4 and 6 respectively, indicates that two of the three values of X/M for column study are greater than obtained in isotherm study indicating better removal in the column study. This is in contrast with the results for Waste II in which the column study X/M value of 0.235 is between the maximum 0.494 and the minimum 0.127, obtained for isotherm study. It is interesting to note that in the column study, for Waste IV, as the residence time increases the removal per unit mass decreases, a phenomenon also observed by Cohen and Kugelman (6) in their studies. This indicates that the determination of an optimum residence time for column operation is essential.

In summary, the characteristic breakthrough curve was exhibited only by the waste that exhibited favorable adsorption pattern. In the case of Waste II, the effluent concentration after the saturation of the bed was lower than the raw waste concentration, which probably increased the removal by some type of filtration mechanism. The residence time is a critical factor for efficient operation of a column.

Regeneration Study

In the regeneration study for Waste II-A and Carbon H, one liter of the

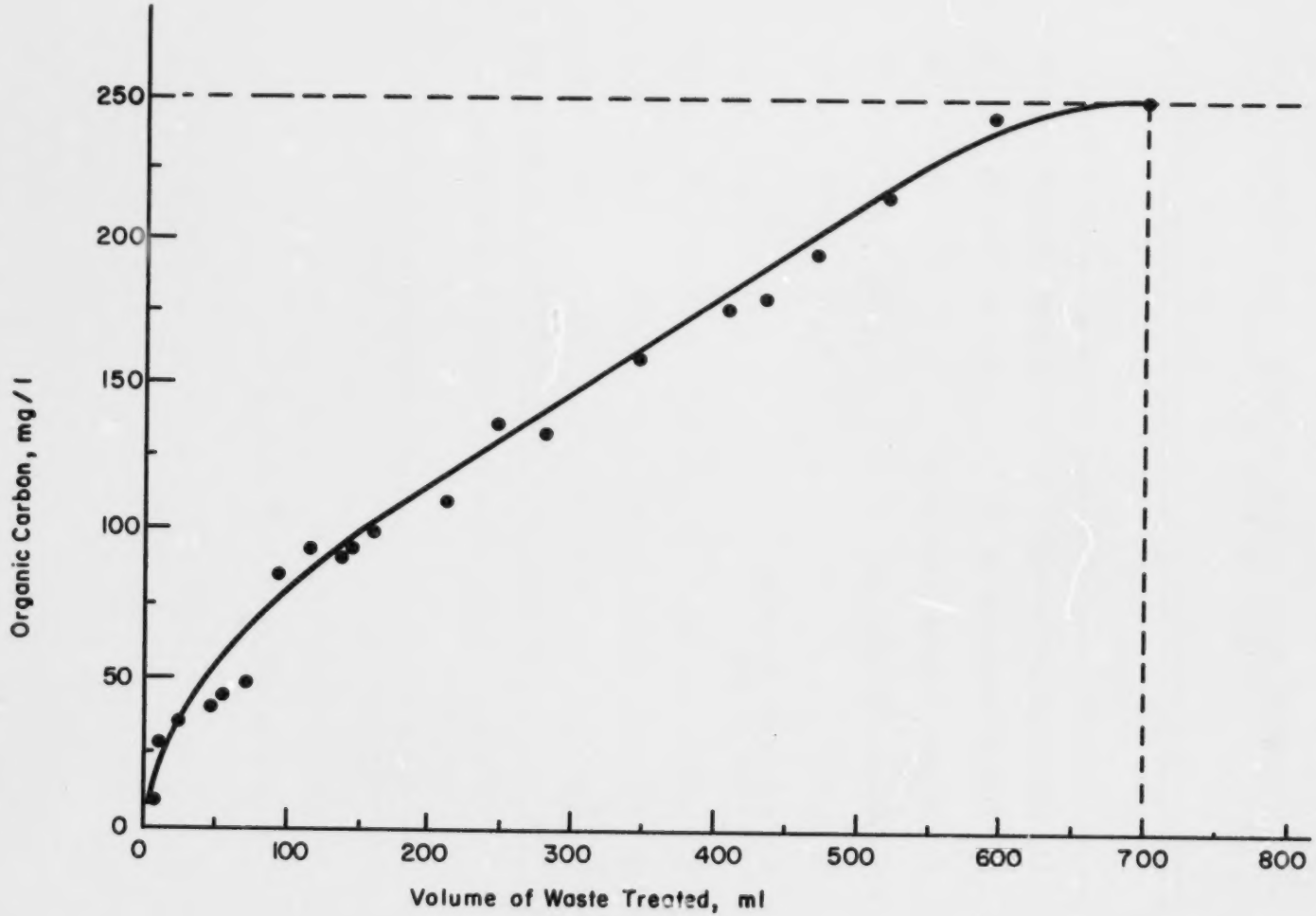


Figure 16. Results of packed column study with Waste IV and Carbon A

TABLE 6

SUMMARY OF THE RESULTS OF THREE PACKED COLUMN STUDIES FOR WASTE IV, CARBON A

Columns	1	2	3
1. Activated Carbon (gm)	2.0385	2.0204	0.3364
2. Time of Operation (hrs)	511:45	511:45	90
3. Volume of Waste Treated (ml)	731	511	526
* 4. Carbon Adsorbed (mg)	93	37.7	277
5. x/M	0.048	0.0184	0.082
** 6. Volume of Activated Carbon (ml)	4.72	4.67	0.779
++ 7. Void Volume (ml)	3.59	3.55	0.592
8. Flow Rate (ml/hr)	1.428	1.00	5.87
+ 9. Residence Time (hrs)	2.52	3.55	0.1

* Obtained from the respective figures by counting squares.

** Volume of activated carbon: weight/0.433, 0.433 being the density.

\+ Void volume/flow rate.

++ Void volume is 76.1 of total volume.

waste was contacted with 3.019 grams of carbon for a period of about 48 hours. During this period the initial concentration of organic carbon, 2585 mg/L, was reduced to 1889 mg/L resulting in overall adsorption of 0.23 grams of organic carbon per gram of activated carbon. The saturated carbon was divided into four parts; one part was dried at 70-80°C and the other three regenerated at 400, 700 and 1000 degrees fahrenheit. After the regeneration of spent carbon, an isotherm study was conducted with 10 ml of waste. The results are presented in Table 7. The Freundlich isotherm model was used to compare the performance of regenerated carbon, Figure 17. It is apparent that an increasing regeneration temperature improves the adsorption pattern. As indicated in Table 8, the parameters E and n increased with temperature, a positive sign that regeneration improved with increasing temperature.

In the study with Waste IV and Carbon B, 4.033 grams of carbon were contacted with two liters of the waste to reach a steady state concentration of 214 mg/L from the initial concentration of 292 mg/L to give an adsorption of 0.0387 grams of organic carbon per gram of activated carbon. The saturated carbon was divided into five parts for regeneration. The regenerated carbon was contacted with 10 ml of waste, the results are presented in Table 9. The linearized form of Freundlich model is also presented in Figure 18.

Comparison of the results of the two studies shows that the system exhibiting favorable adsorption, Waste II-A, requires a high temperature of regeneration and more energy expended for regeneration. In the case of Waste II-A, the optimum temperature of regeneration was higher than 1000°F, but for Waste IV, it is around 600°F. Therefore, it is necessary that the optimum temperature of regeneration be established for every system. A higher than optimum temperature would probably reduce the efficiency of the process and also damage the carbon.

TABLE 7

RESULTS OF REGENERATION STUDY WASTE II-A: CARBON B

Virgin				0°F				400°F			
M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X
0	2345	-	-	0	2295	0	0	0	2245	-	-
550	2225	120	0.218	480	2295	0	0	590	2185	60	0.1018
1040	2125	220	0.216	1050	2295	0	0	970	2155	90	0.0929
1930	-	-	-	2060	2295	0	0	1970	2065	180	0.0914
3100	1765	580	0.187	3020	2295	0	0	3170	1975	270	0.0852
4020	1625	720	0.179	4140	2295	0	0	4110	1915	330	0.0803
5410	1385	960	0.177	5000	2295	0	0	5210	1855	390	0.0748
6170	1245	1100	0.178	6150	2295	0	0	6150	1815	430	0.0699
7270	1085	1260	0.173	7150	2295	0	0	7260	1765	480	0.0662
700°F				1000°F							
0	2245	-	-	0	2295	-	-				
450	2185	60	0.133	560	2215	80	0.143				
1050	2115	130	0.124	1080	2145	150	0.139				
1970	2005	240	0.122	2020	-	-	-				
3210	1875	370	0.115	3080	1925	370	0.120				
3990	1805	440	0.110	4010	1845	450	0.112				
4980	1755	490	0.098	4930	1705	490	0.100				
6120	1725	520	0.085	6250	1665	630	0.101				
7330	1645	600	0.082	7680	1385	910	0.118				

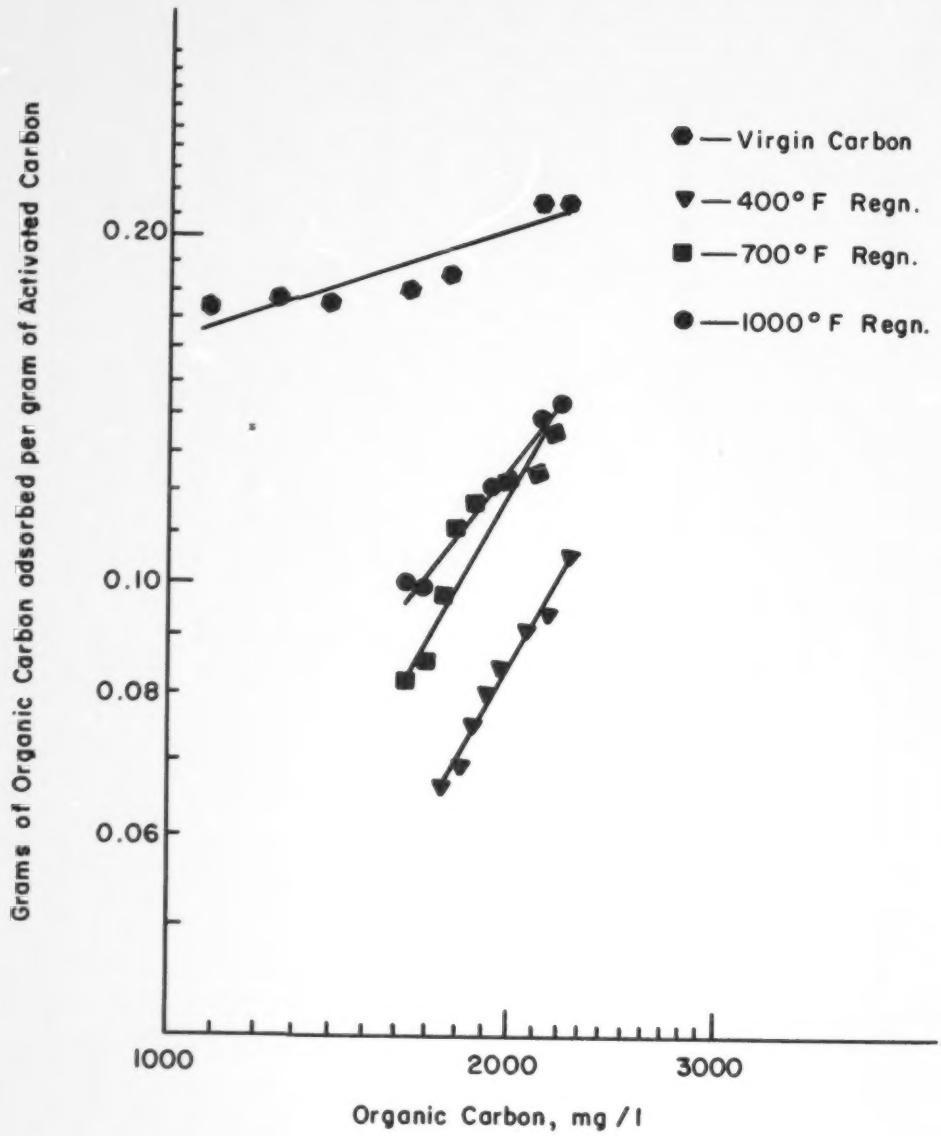


Figure 17. Effect of temperature on regeneration for Waste II-A and Carbon B.

TABLE 8

Co-efficients and Exponents of Freundlich Isotherm Model, Equation (3) Evaluated From the Results of Regeneration Study for Wastes II-A and IV With Carbon B

Waste II-A - Carbon B

Freundlich Model Parameter	Virgin	Regeneration Temperature			
		$0^{o}F$	$400^{o}F$	$700^{o}F$	$1000^{o}F$
E	1.7108×10^{-2}		8.734×10^{-8}	1.77×10^{-7}	7.637×10^{-6}
n	3.0684		0.5512	0.5663	0.7830

Waste IV - Carbon B

Freundlich Model Parameter	Virgin	Regeneration Temperature				
		$0^{o}F$	$400^{o}F$	$600^{o}F$	$800^{o}F$	$1000^{o}F$
E	1.048×10^{-5}	0.8989	2.03×10^{-5}	35.79×10^{-5}	0.097×10^{-5}	0.379×10^{-5}
n	0.6434	-1.1551	0.7641	1.2977	0.535	0.6298

TABLE 9

RESULTS OF REGENERATION STUDY WASTE IV: CARBON B

Virgin Carbon				0° Regeneration				400°F			
M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X	M	Eqm. Conc.	x	X
0	264	-	-	0	290	-	-	0	330	-	-
2040	189	75	0.0368	520	290	0	0	570	310	20	0.0351
4152	159	105	0.0253	1000	290	0	0	1160	292	38	0.0328
5228	135	129	0.0247	2200	276	14	0.0064	2020	264	66	0.0327
6000	132	132	0.0220	3040	268	22	0.0072	3150	242	88	0.0279
7112	130	134	0.0188	4090	262	28	0.0068	4050	224	106	0.0262
7944	127	147	0.0185	5130	256	44	0.0086	5060	212	118	0.0233
				6030	256	44	0.0073	6140	204	126	0.0205
				7130	246	54	0.0076	6950	200	130	0.0187
600°F				800°F				1000°F			
0	290	0	0	0	330	-	-	0	345	-	-
610	275	15	0.0246	530	304	26	0.0491	490	340	5	0.0102
1100	262	28	0.0255	1040	290	40	0.0385	1080	334	11	0.0102
2090	234	56	0.0268	1980	274	56	0.0283	2080	312	33	0.0159
3110	216	74	0.0238	3020	248	82	0.0272	3130	264	81	0.0259
4270	196	94	0.0220	4020	224	106	0.0264	4070	248	97	0.0238
5170	186	104	0.0201	5070	212	118	0.0233	5000	232	113	0.0226
6140	176	114	0.0186	6150	202	128	0.0208	6060	220	125	0.0206
7160	166	124	0.0173	7760	196	134	0.0173	7140	216	129	0.0184

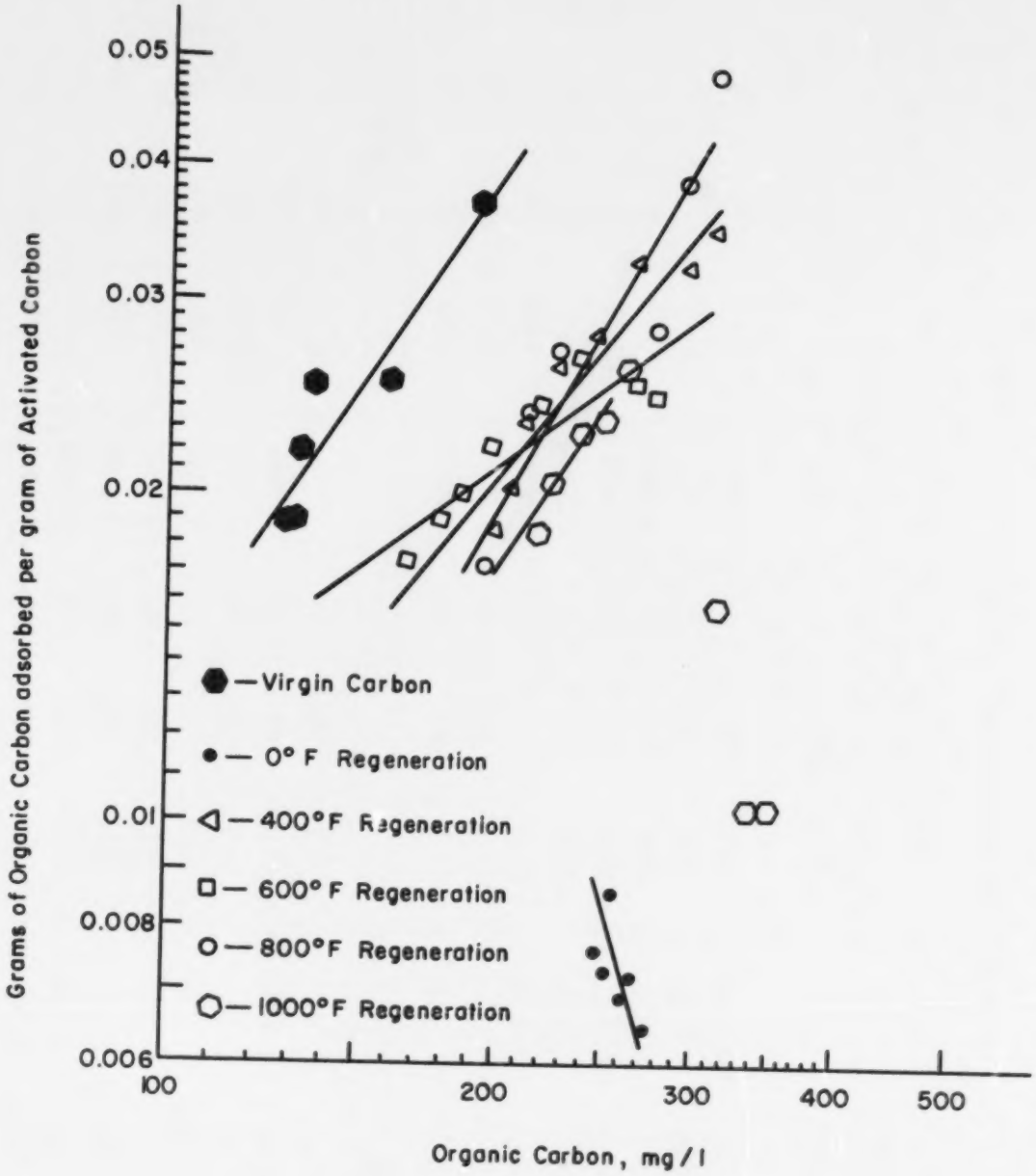


Figure 18. Effect of temperature on regeneration of Waste IV and Carbon B.

It should be indicated that even at an optimum regeneration temperature, the regenerated carbon did not match the performance of virgin carbon. Although it is hard to pin point the reason within the limitations of this study; a host of reasons can be cited in which the damage to pore structure of carbon due to thermal stress is the most significant.

In summary, the optimum temperature of regeneration for each system should be established. Even regeneration at optimum temperature would not return the carbon to the performance level of virgin carbon, which is probably due to the damage caused by thermal stress to the pore structure.

SECTION 7

VACUUM-THERMAL REGENERATION OF ACTIVATED CARBON

The purpose of this study was to determine the specific regeneration response of activated carbon, saturated with selected sorbates, to high temperature vacuum regeneration.

Conventionally spent activated carbon is regenerated by exposure to high temperature conditions in multiple hearth furnaces or rotary kiln devices. In this process, carrier gases such as carbon dioxide and stam are used to prevent oxidation of the carbon sorbent. The role of the carrier gas, in terms of protecting the carbon sorbent, is well defined; however, the role of the carrier gas in terms of regeneration and/or reactivation is not defined. In order to minimize the effect of the carrier gas on thermal regeneration, this study was designed on the basis of using vacuum thermal regeneration techniques.

Prior to development of special vacuum thermal regeneration equipment, samples of various commercial grades of activated carbon saturated with petrochemical waste and methylene blue sorbates were prepared. These samples were subjected to vacuum differential thermal analysis (DTA). Following differential thermal analysis, the samples were examined for sorption capacity. Results of this study established that vacuum thermal regeneration was possible and potentially promising.

Consideration of the factors involved in testing carbon sorbates, together with the relatively large amounts of activated carbon required, showed that a special vacuum furnace device would be required. The DTA apparatus was capable of containing a 50 mg sample; however, 50 gram samples of material were required for sorption, regeneration, and analysis.

The sorbates selected for this study were iodine, methylene blue, para-

chlorophenol, and a petrochemical waste material. Iodine is a standard sorbate material routinely used to evaluate activated carbon sorption capacity and micro pore capacity. In practice, activated carbon materials which exhibit an iodine affinity of 600 mg per gram of carbon, or greater, as determined by a standard solution exposure and contact procedures, are considered to be high quality sorbent materials. It is generally agreed that the iodine sorption capacity of activated carbon is a measure of the micropore spaces (35, 36). Usually the numerical value of the iodine number for an activated carbon sorbent is very similar to the surface area per unit mass value. Thus, for very porous activated carbon materials, the iodine number and the surface area per unit mass (m^3/gm) values are nearly the same. The established nature of iodine sorption by activated carbon was the first basis for selecting this material, however, iodine has an additional characteristic which favored inclusion in this study. It is an inorganic material which shows well defined sharp melting and boiling points at 113°C and 184°C, respectively. Moreover, it is only slightly soluble in water (<162 mg/liter at 20°C) and sublimes, without melting, below a pressure of 100 mm Hg. In addition, this element has a relatively high heat of vaporization value - 10,388 cal/mole.

Methylene blue was included in this study because it is also a standard material used in sorption studies. The major reason for using methylene blue, in activated carbon sorption studies, is related to the optical properties of this substance. Dilute solutions of methylene blue exhibit a pure blue color which conforms to the Beer-Lambert relationship at 665 millimicrons. Thus, it is convenient and easy to measure the sorption uptake of methylene blue by colorimetric measurement. Traditionally methylene blue has been used in sanitary engineering to evaluate sorption and the relative stability of biooxidation processes. Methylene blue is a relatively large molecule having a

molecular weight value of 320. Probably the most interesting feature of methylene blue is that it decomposes before melting.

The third sorbate material selected for this study was parachlorophenol. Generally the para-chlorophenol molecule is considered to be similar to many components found in organic chemical and petrochemical trade wastes. Para-chlorophenol is a dichloro derivative of benzene which is slightly soluble in water and is a solid at 23°C. This material exhibits a sharp melting point at 42°C and boils at 217°C. In contrast to methylene blue and iodine, para-chlorophenol is a moderately soluble low molecular weight material possessing a relatively high boiling point.

The fourth sorbate material selected for this study was a petrochemical waste material. Specifically, the petrochemical waste material was collected from a cold temperature quenching operation waste stream by representatives of Gulf South Research Institute. The waste sample was highly colored, had a COD value of 10,180 mg/liter, and contained 1,810 mg/liter dissolved organic carbon. Chloride concentration of the waste was 14 mg/liter and the pH value was 9.7. This waste material was representative of a specific petrochemical waste stream containing relatively large quantities of benzene derivatives.

Activated carbon materials used in this study were Filtrasorb 400[1] and Nuchar WVL[2]. Preliminary laboratory study showed that both carbon materials were effective sorbents for the selected sorbates and exhibited stable response to high temperature exposure. Prior to application, stock quantities of the selected carbon materials were ground up and sieved to pass 40 mesh size, soaked in distilled water, and dried at 103°C for 24 hours.

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[1]Product of Calgon Chemical Co., Pittsburgh, Pennsylvania
[2]Product of Westvaco Chemical Division, Covington, Virginia

Analysis of the organic sorbate concentration was accomplished on the basis of total organic carbon using a Beckman Carbon Analyzer instrument[1]. Procedure developed for determining the total organic carbon concentration of para-chlorophenol, methylene blue, and the petrochemical waste consisted of removing a 1.0 ml portion of the carbon-wast solution, diluting to 100 ml with distilled water, acidification with HNO_3 to pH value of 2, and the injection of a small sample (10-50 microliter) into the carbon analyzer. The carbon analyzer instrument was standardized just prior to use with standard glucose solutions.

Residual iodine concentration was measured by starch-iodine titration using sodium thiosulfate as a titrant (35). The complete detailed analysis of iodine and iodine number determination are presented in Appendix B.

The laboratory procedure used to establish sorption consisted of contacting the sorbate solutions with varying amount of activated carbon and determining the change in sorbate concentration with time. Specifically this procedure involved contacting 1.0, 3.0, 5.0, 7.0, 10.0, 20.0, 50.0, 100 and 250 milligram portions of activated carbon with 100 ml of sorbate solutions. The sorbate solutions were prepared and applied in the following concentrations: iodine 1000 mg/liter, para-chlorophenol 1000 mg/liter, methylene blue 100 mg/liter and petrochemical waste 1,810 mg/liter organic carbon. In practice, weighed amounts of activated carbon were transferred to a series of 125 ml Erlenmeyer flasks containing 100 ml of sorbate solution. The activated carbon-sorbate solution mixture was then placed in a 22°C temperature controlled modified Warburg apparatus. Aliquot samples of the incubated solutions were removed by pipetting at five hour intervals

[1]Product of Beckman Instruments, Inc., Fullerton, California

diluted with distilled water and reserved for analysis. Following determination of sorption equilibrium, samples of the respective mixture (activated carbon-sorbate) were prepared for thermal regeneration.

Preliminary study showed that all sorbate materials reached sorption equilibrium in 24 hours or less. On the basis of this determination, all of the experimental solution mixtures were subjected to a 24 hour contact period. A wide range of carbon to sorbate ratios and concentrations were contacted in the preliminary study and representative loading values of 0.25, 0.75, 0.90 gms of sorbate/gm of carbon were used for the balance of the investigation.

Thermal regeneration was provided by exposing 1 gram portions of sorbate-carbon mixtures (spent carbon) to temperatures ranging from 200°F to 1400°F in a vacuum tube furnace. The procedure of thermal regeneration involved transferring weighed samples of activated carbon-sorbate mixtures to a small ceramic sample boat. The ceramic sample boat and contents were then located in the center of a 1.5 inch diameter 32 inch long ceramic furnace combustion tube. A contact thermocouple was placed in the sample boat just prior to evacuating the combustion tube. After location of the sample, the combustion tube was sealed with rubber plugs and evacuated to 50 mm Hg pressure. Temperature of the sample was monitored continuously with a cromel alumel thermocouple attached to a Minneapolis-Honeywell, Model 2H-11, strip chart recorder[1]. Pressure in the combustion tube was determined using an electronic vacuum gauge. A sketch of the experimental equipment is shown in Figure 19.

Following completion of the heating regime, the sample boat and contents

[1]Product of Minneapolis-Honeywell Corporation, Pittsburgh, Pennsylvania

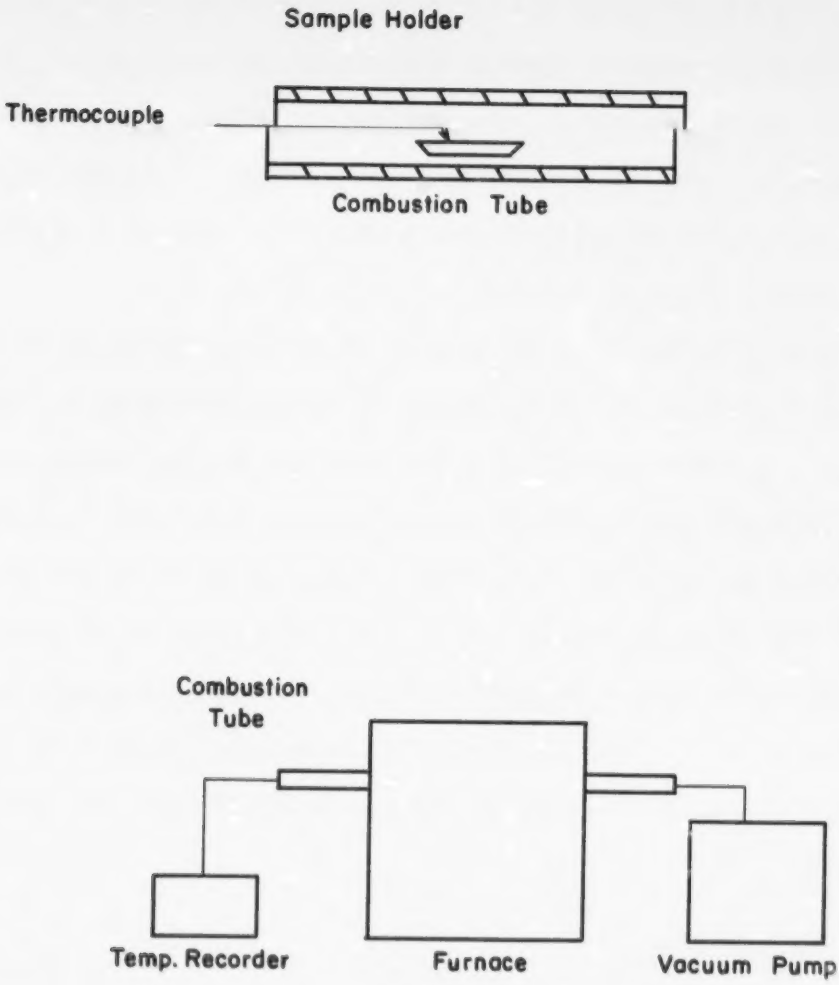

Figure 19. Experimental carbon regeneration equipment.

were permitted to cool to ambient temperature in the 50 mm Hg pressure combustion tube. Samples of the thermally regenerated mixture were placed in a dessicator and prepared for sorption study.

Determination of the effect of thermal regeneration was accomplished by determining the sorption loading achieved by the regenerated carbon sorbent. This operation involved exposure of a weighed portion of the regenerated sorbent to various concentrations of sorbate. The same procedure, sorbate, equipment, and analysis were used in this test as in the initial sorption test.

It should be noted that all samples of activated carbon sorbate mixtures were heated in a 50 mm Hg vacuum. A control manometer was not used to control the vacuum; the 50 mm Hg pressure was the equilibrium pressure attained with the porous ceramic combustion tube apparatus. Preliminary experimentation showed that this pressure was sufficient to prevent oxidation of the activated carbon. All samples of the activated carbon sorbate mixture were heated in ceramic sample boats and were spread out over the total surface of the boat in order to promote good heat transfer. The location of the sample boat in the furnace combustion tube is shown in Figure 19.

Results and Discussion

Results of the initial sorption regeneration study, using Filtrasorb #400 activated carbon and methylene blue dye, showed that increased temperature favored regeneration response. The specific response of Filtrasorb #400 activated carbon samples, exposed to temperatures ranging from 220°F to 1200°F, is shown in Figure 20. The effect of sorption capacity loading, in terms of grams of sorbate sorbed per gram of carbon, is displayed in Figure 20 as four separate curves. The sorption regeneration response, for

each sample, was determined and tabulated by comparison with virgin Filtrasorb #400 activated carbon sorption values and plotted as a regeneration ratio (Rr) value. The regeneration ratio value was calculated using the following relationship.

$$Rr = \frac{(X/M)\ reg}{(X/M)\ virg}$$

where

Rx = regeneration ratio

X = mass of sorbate (methylene blue), grams

M = mass of sorbent (activated carbon), grams

This procedure permitted direct evaluation of regeneration response in terms of experimentally determined sorption capacity values for Filtrasorb #400 virgin activated carbon.

The sorption loading values and their associated thermal regeneration response, in terms of Rr values in the temperature range 200°F, describe a family of smooth curves. Each sorption capacity curve showed a linear increase in sorption capacity from 200°F to about 800°F each curve exhibited a rapid increase in sorption capacity which continued to 1000°F. The curves show that, in the 1000°F to 1200°F region, the increase in sorption capacity was slight. Each of the regeneration ratio versus temperature curves is specific with respect to the initial regeneration ration (Y axis intercept) and rate of change in the 200°F to 800°F region. The initial sorption values (plotted on the ambient temperature scale value) represent the used sorption capacity of Filtrasorb #400 virgin carbon and the slope of each curve describes how rapidly the used capacity is regained as a function of temperature.

The most interesting features of the curve, shown in Figure 20, is the threshold response to temperatures exhibited by all the curves at about 800°F and the convergence of the curves at 1200°F. These conditions predicate tnat

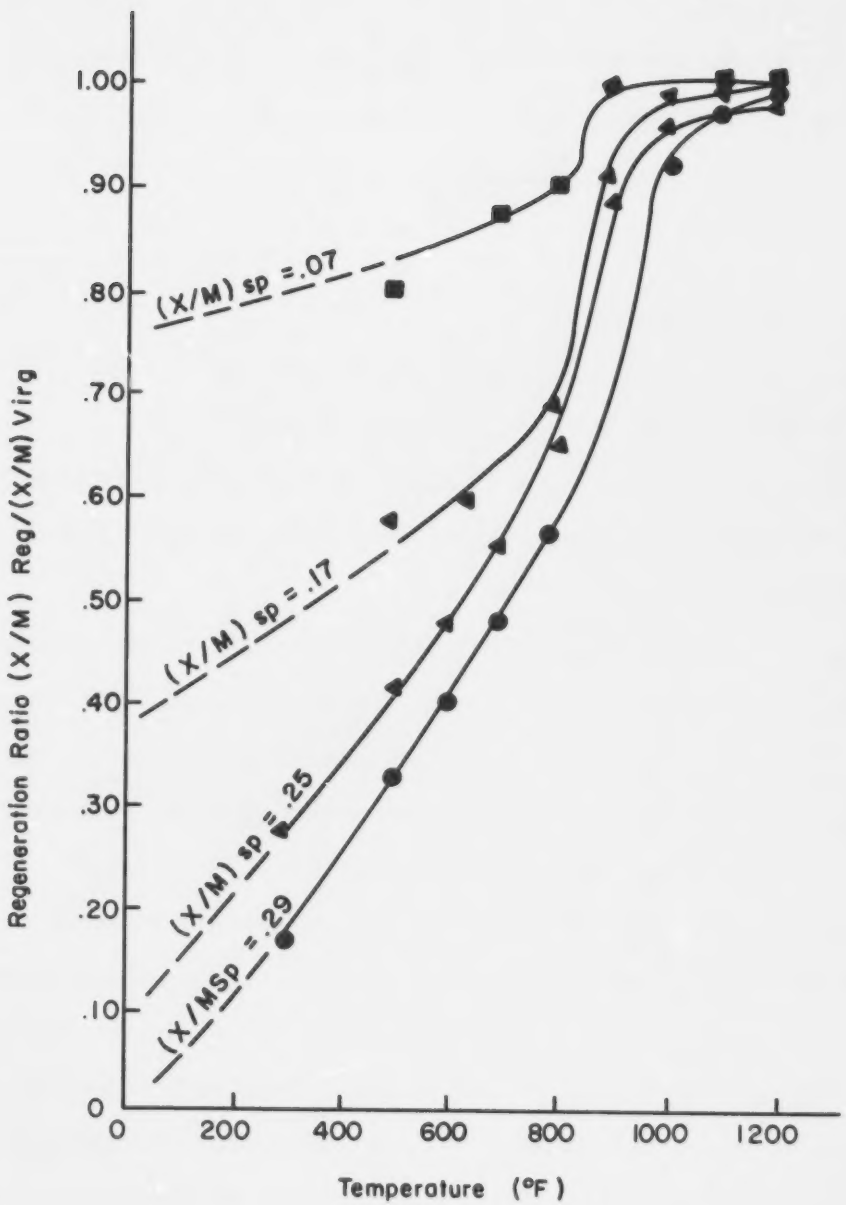

Figure 20. Effect of specific sorption capacity on regeneration.

800°F is a realistic minimum value for thermal vacuum regeneration and show that maximum gain in regeneration capacity per degree temperature is achieved in the 800°F to 1000°F range. Further consideration of Figure 20 suggests that rate of response, i.e., the increase in regenerated capacity as a function of temperature, increased with increasing loading capacity. This feature was selected for additional study and is discussed in the following section.

Plotting the data displayed in Figure 20 as regeneration ratio versus specific sorption capacity, using temperature as an independent variable, yielded the family of curves shown in Figure 21. The term, specific sorption, developed for use in this analysis was calculated by determining the difference in sorption capacity occasioned by saturation with methylene blue. Thus, the specific sorption values plotted in Figure 21 represent the spent sorption capacity of the Filtrasorb #400 sorbent.

An interesting finding, illustrated in Figure 21 is the linear relationship of regeneration gain versus temperature exhibited by each curve. The effect of specific sorption capacity is shown to be most pronounced in the low temperature region (300°F - 500°F) decreasing in the 800° region and decreasing further in the 1000°F to 1200°F region. The most interesting feature displayed by the data plotted in Figure 21 is the linear relationship of temperature, regeneration capacity, and specific sorption capacity. The relationship between sorption capacity and regeneration ratio is described by the following

$$Rr = 1 - \left(\frac{X}{m}\right) sp\ Mt$$

where

Rr = regeneration ratio

$\left(\frac{X}{m}\right)sp$ = specific sorption capacity, mg/mg

Mt = temperature rate coefficient.

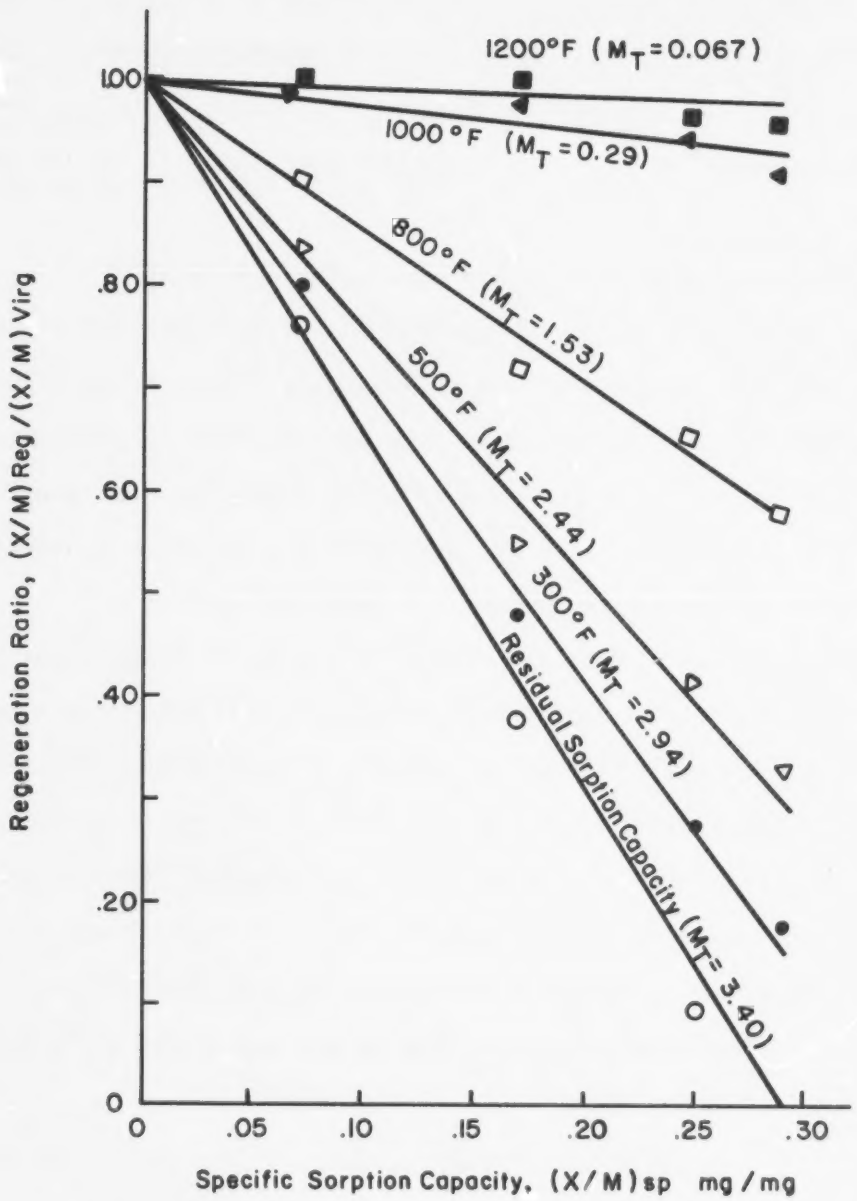

Figure 21. Effect of specific sorption capacity on regeneration.

The temperature coefficient term, Mt, is an empirical constant and specific for each waste sorbate-sorbent combination, temperature region, and sorbate loading value. Seemingly the Mt term is somewhat similar to a rate constant. A test of this idea was developed by plotting Mt values versus temperature, Figure 22. Although the curve shown in Figure 22 exhibits significant curvature, it indicates a proportional relationship between Mt and temperature in the 70°F to 800°F region. Moreover, the shape of the curve presented in Figure 22 indicates that the Mt term depicts the sorbate loss. Consequently direct comparison of the Mt and Rr values for a specific sorbate loading value, should show similar changes. The curves shown in Figure 23 illustrate that this relationship is valid. In the 70°F to 1200°F region, the Mt versus temperature curve is an inverse reflection of the Rr versus temperature curve. Thus, the Mt term is a measure of sorbate removal and the Rr term is a measure of regeneration.

Collectively the results of the Filtrasorb #400 - methylene blue study showed that thermal regeneration proceeded in a regular progression dependent upon temperature and sorption loading. Moreover, the gain in regenerated sorption capacity appeared to be directly related to the specific sorption capacity. As an aid to development of data analysis, a composite term, regeneration efficiency (Re), was devised. The purpose of introducing the Re term is to minimize the number of factors and to develop and expression relating regeneration response and temperature. The Re expression combines the former Rr and specific sorption loading term into a single expression defined by the following relationship

$$Re = \frac{(X/M)\ reg - (X/M)_o}{(X/M)\ virg}$$

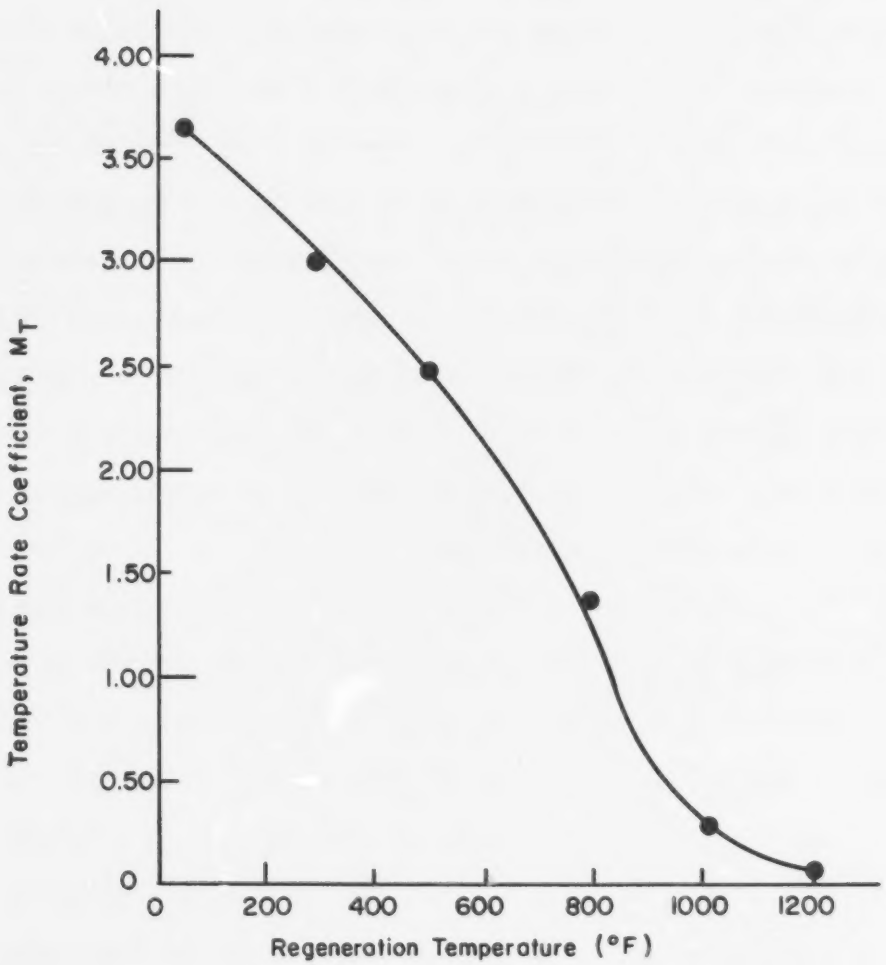

Figure 22. Temperature rate coefficient versus temperature.

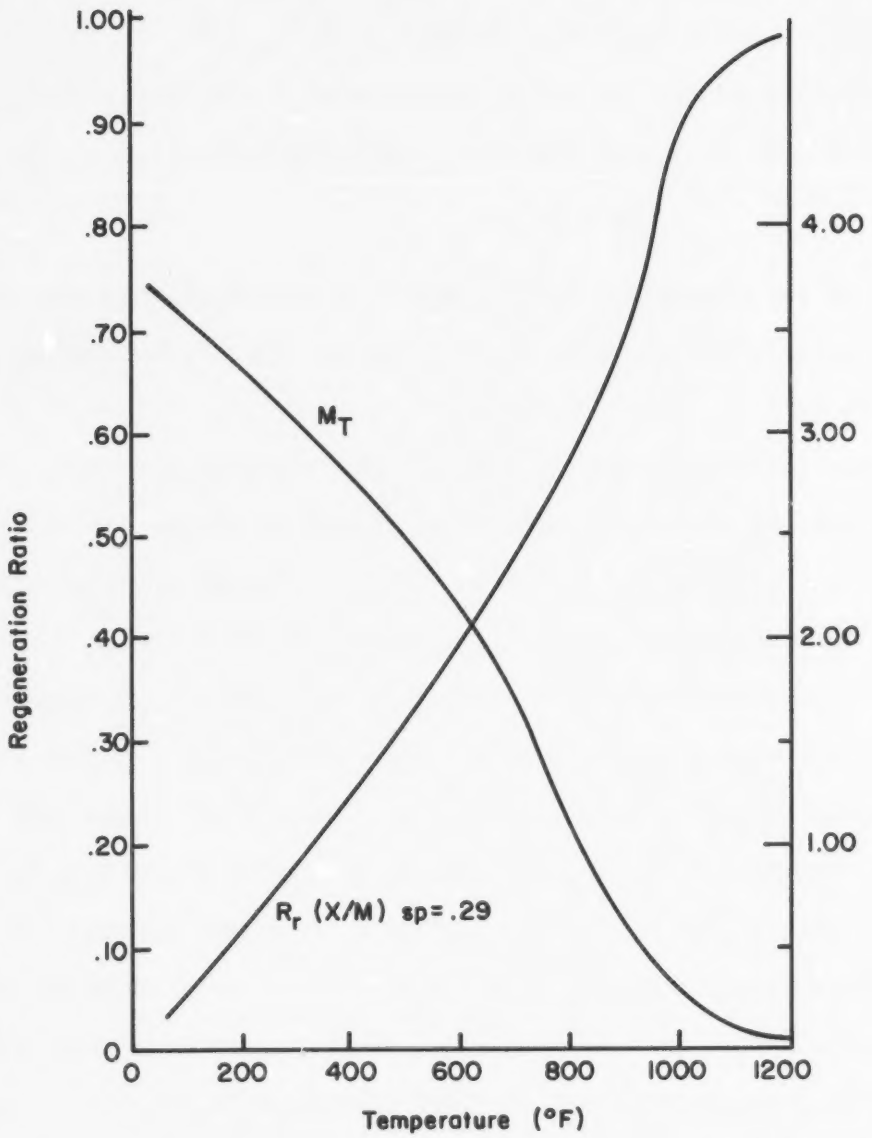

Figure 23. Comparison of M_T and regeneration response.

where

X/M reg = regenerated sorption capacity, gm/gm

X/M virg = virgin carbon sorption capacity, gm/gm

$(X/M)_o$ = residual sorption capacity, gm/gm

The relationship between the initial measurement of sorption, regeneration, regeneration ratio (Rr), and regeneration efficiency is

$$Re = Rr - Rr_o$$

where Rr_o is the regeneration ratio normalized to residual sorption capacity. The above relationship requires that Re equal Rr when the residual sorption capacity is zero.

A graphical presentation of regeneration efficiency (Re) versus temperature for methylene blue sorbed on Filtrasorb #400 and Nuchar WVL activated carbons is shown in Figure 24. The most interesting and potentially useful finding illustrated in Figure 24 is the similar linear increase in regeneration efficiency as a function of temperature exhibited by Filtrasorb #400 and Nuchar WVL activated carbon. Both sorbent materials show a similar response to the thermal regeneration response curve. Specifically, Nuchar WVL material showed an increase of 53 percent in the 100°F to 500°F temperature ranges; whereas, Filtrasorb #400 material evidenced a 54 percent increase. The one percent difference in response is well within the range of experimental error and is probably not significant. It is apparent that both sorbent materials increased in sorption efficiency at about the same rate.

The general shape of the thermal regeneration response curves, shown in Figure 24, suggests that there is a dissimilar response characteristic of each type of carbon. Generally, the inflection point common to each sorbent, 500°F for Nuchar WVL and 800°F for Filtrasorb #400, is the threshold temperature value for thermal regeneration, the specific response of each carbon at

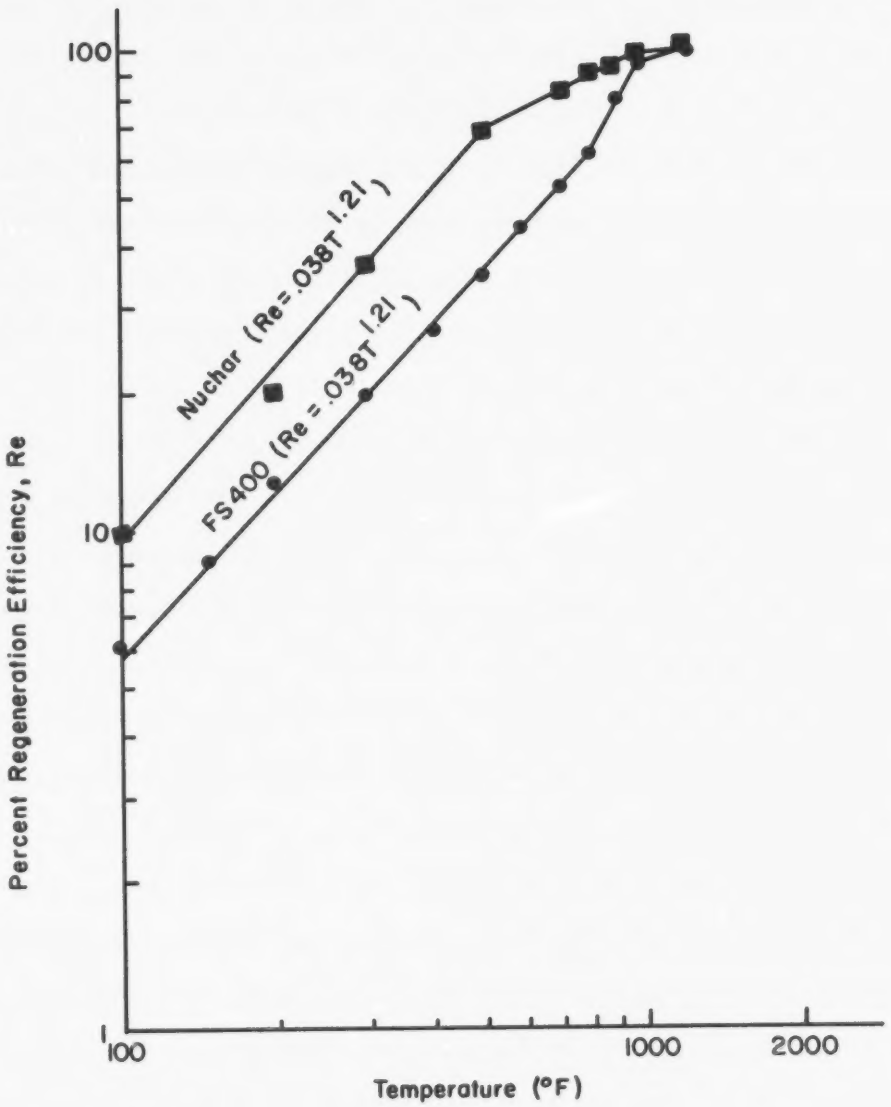

Figure 24. Methylene-blue regeneration efficiency.

temperatures greater than the threshold value are different. The Filtrasorb #400 material showed a slightly increased rate of regeneration response in the high temperature region, whereas, the Nuchar WVL material showed a decreased rate of response. In both cases the change from the initial linear course is slight and both curves coincide at about 1000°F.

In order to test the fidelity of the response pattern and the data analysis process, the thermal response data for iodine, petrochemical waste, and para-chlorophenol were examined. Results of this operation, Figures 25, 26, and 27, show that the thermal regeneration response was similar to the response pattern of methylene blue.

All of the thermal regeneration response curves shown in Figures 25, 26, and 27, describe a family of curves very similar to the methylene blue thermal regeneration prototype (Figure 24). There is an obvious upward displacement of the iodine, parachlorophenol and petrochemical waste curves directly proportional to the specific sorption capacity of each material. The most atypical regeneration response pattern is illustrated by iodine. Iodine is a unique material in that it is not decomposed during thermal regeneration, rather it vaporizes. Consequently, the response pattern of iodine is indicative of the behavior of a volatile non-reactive sorbate. On this basis, it seems probable that the initial portion of each thermal regeneration response curve illustrates the volative loss of sorbate during thermal regeneration.

Comparison of the thermal regeneration response patterns shown in Figures 24, 25, 26, and 27, reveals consistent response. In terms of temperature required for regeneration, the carbon-iodine samples achieved full regeneration at about 300°F, whereas, carbon-para-chlorophenol, carbon-methylene blue, and carbon-petrochemical wastes required 800°F, 1000°F and 1000°F resepctively. The rate of regeneration response exhibited by each of the sorbate materials was not related to the threshold temperature. Comparison of the rate values

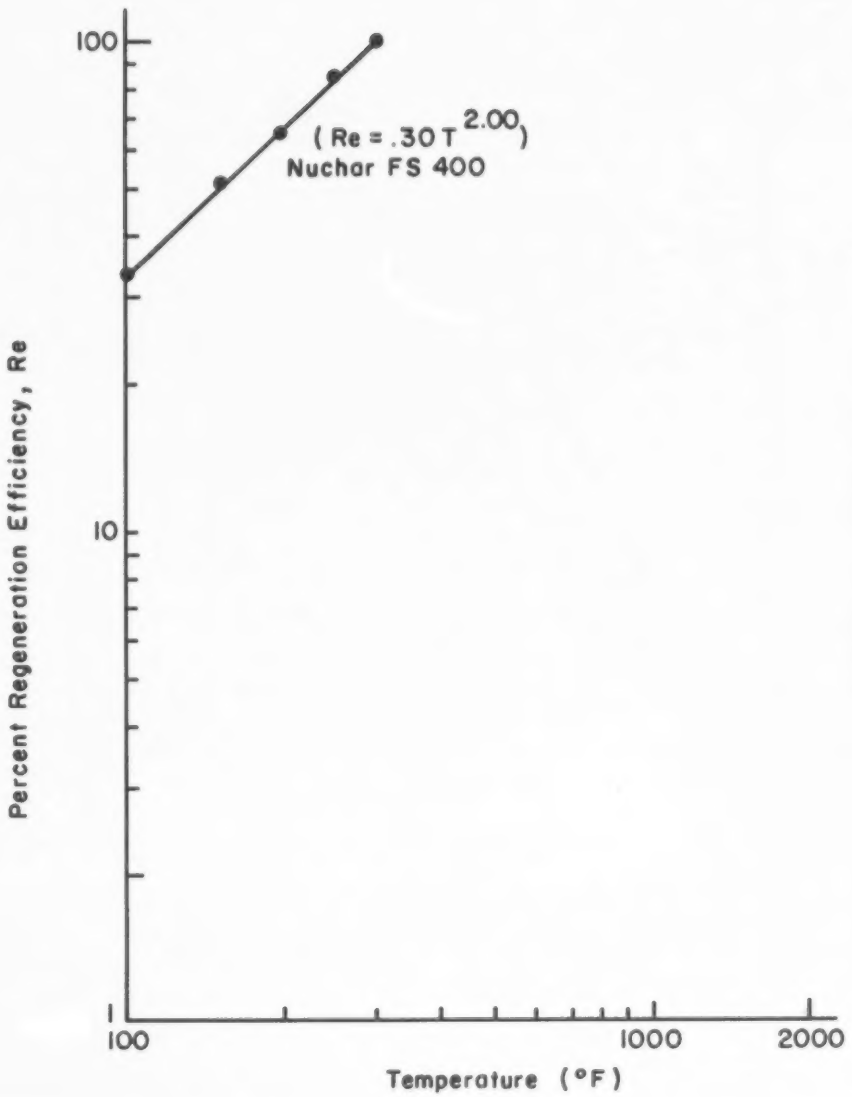

Figure 25. Iodine regeneration efficiency.

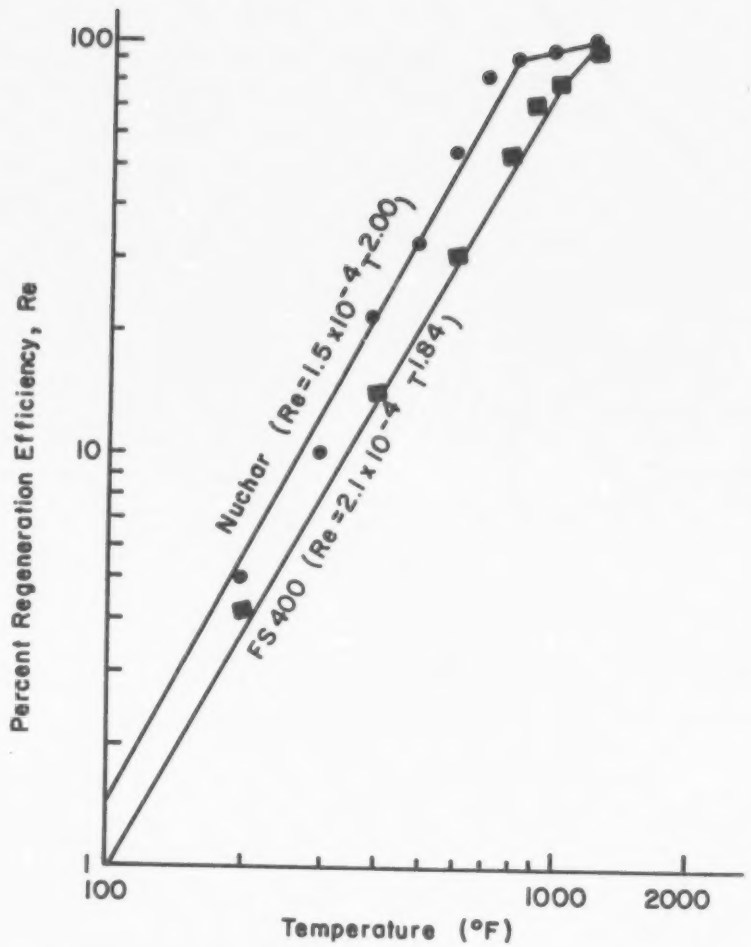

Figure 26. Petrochemical Waste Regeneration Efficiency

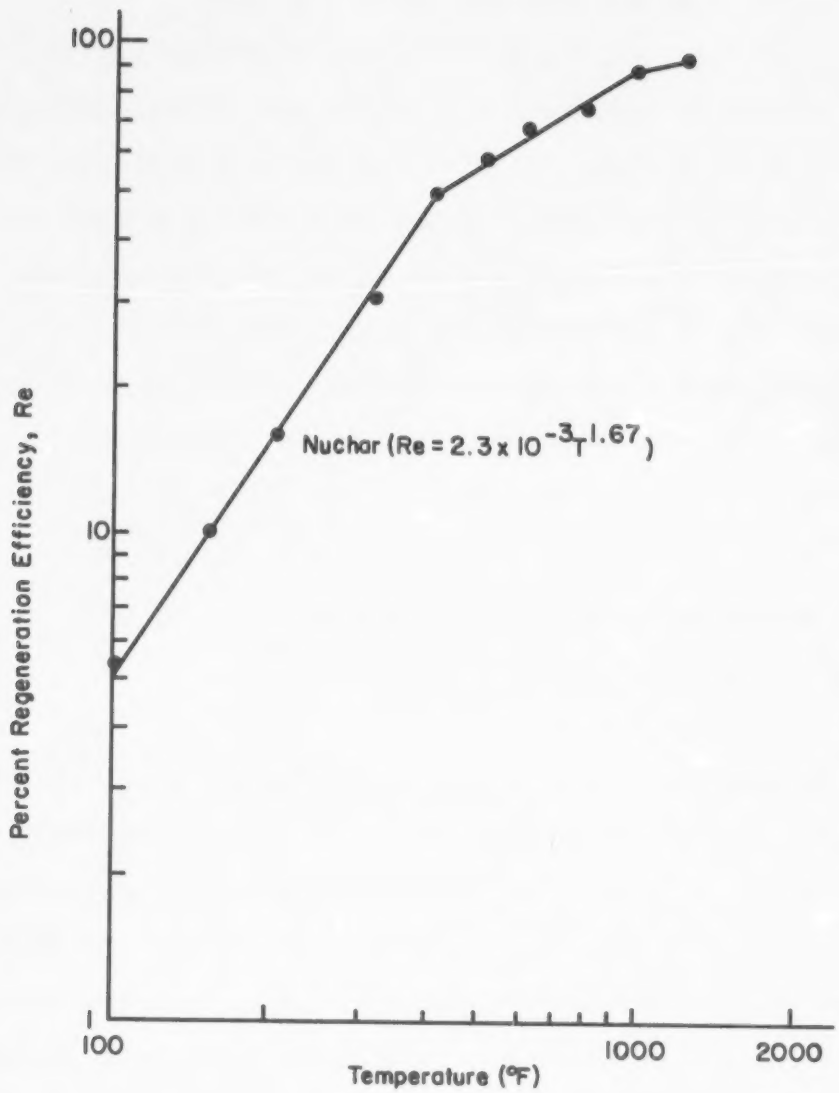

Figure 27. Chlorophenol Regeneration Efficiency

listed in Figures 24, 25, 26, and 27 shows that the carbon-petrochemical waste material regenerated at the fastest rate, followed in order by para-chlorophenol, methylene blue, and iodine. The specific rate of thermal regeneration, as a function of temperature, is apparently unique for each waste sorbate; however, the rate values for each waste-carbon combination range from 1.21 to 2.00. The differences exhibited by the rate values are not particularly distinctive. Rather, the similarity in these values suggests that the initial portion of the thermal regeneration process proceeds at about the same rate irrespective of the sorbate materials.

On the basis of the above considerations the vacuum thermal regeneration response can be described by the following relationship

$$Re = KT^n$$

where

Re = regeneration efficiency, percent

K and n = empirical constants

T = temperature, °F.

The above relationship predicates that vacuum thermal regeneration is an exponential function of temperature. The empirical constants associated with temperature, K and n, are directly proportional to specific sorption values and rate of regeneration response, respectively. The relationship proposed in this equation is approximate since it does not account for the inflection point which occurs at the threshold temperature. However, the inflection point, or threshold temperature, is specific and unique for each waste sorbate-carbon combination. Moreover, the equation is significant in that it shows: (1) overall response, in terms of thermal regeneration response, as an exponential function of temperature and (2) the relationship between specific sorption capacity, and/or loading rate of regeneration response.

SECTION 8

DIFFERENTIAL THERMAL ANALYSIS OF ACTIVATED CARBON REGENERATION

The purpose of this portion of the study was to determine if differential thermal analysis could be used to evaluate activated carbon sorption in terms of temperature and diagnostic exothermic-endothermic reactions.

Activated carbon is a proprietary material and the specific physicochemical reactions requisite to activation are considered to be well guarded trade secrets. Regeneration of spent activated carbon has been achieved using a variety of processes and techniques ranging from solvent extraction to high temperature pyrolysis. The mechanism of thermal regeneration of activated carbon is probably related to activation since both processes are accomplished by heat treatment. Ideally the thermal regeneration of spent activated carbon provides a material for reapplication with the same sorption affinity and capacity as the parent material. Field and laboratory investigations have shown that thermally regenerated activated carbon achieves about 95 percent original sorption capacity per regeneration cycle together with a 5 percent loss of material. In general, the behavior and characteristics of the regenerated carbon are very similar to virgin activated carbon except for increased density of the regenerated carbon.

The most significant problem associated with the large scale application of activated carbon is determination of sorption capacity depletion and regeneration response. Traditionally sorption capacity has been determined by analysis of sorbate solution rather than by direct analysis of the sorbent.

The major interest in this study was directed toward development of analytical procedures based on differential thermal analysis (DTA) and thermal characteristics of the activated carbon sorbate which could be used to detail sorption reactions and/or thermal regeneration. In order to minimize the complexity

of thermal regeneration a basic low pressure thermal regeneration procedure was employed in this study.

Differential thermal analysis (DTA) is a unique form of analysis. In concept, DTA produces a series of patterns which represent the enthalpic reactions specific to selected materials or substances during heating or cooling. In this context, DTA is basically a thermal spectrometer, since the output data usually consists of a series of peaks representing intensity vs thermal energy level. Previous study of DTA has demonstrated that the enthalpic changes or reaction exhibited by samples of pure compounds, materials and mixtures vs. a stable inert thermal standard such as SiO_2 constitute unique qualitative characteristics of the sample. Moreover the quantitative characteristics, such as sample mass or activity are frequently proportional to peak area. Thus DTA is potentially useful for detailing the qualitative-quantitative features of sample materials in a single determination.

The basic components of DTA are; thermal detector, signal amplifier, variable rate of heating furnace and data display system. Most of the commercially available DTA machines provide a variable rate of heating furnace and direct data display. Usually the data output is protrayed as a thermogram, a series of endothermic-exothernic peaks plotted against temperature of the furnace. The basic differences in DTA machines are; the quality of construction, design of the furnace temperature control (heating rate) and data display system design. Basic DTA machines are designed to directly record temperature differences between sample and standard as a function of fixed heating rates; whereas, research DTA machines are equipped with variable heating rate controls and provision for heating samples under low pressure (vacuum) and inert gas atmospheres. In addition, the research machines provide data output via an XY recorder. The advantage of the XY recorder system is that the temperature differences (delta temperature - ΔT) is plotted

directly as a function of the reference standard.

Differential thermal analysis was selected for application to this study because it offered the following advantages:

1) Provided a qualitative - quantitative method for monitoring thermal reactions related to sorption and thermal regeneration.

2) All of the requisite parameters relative to thermal regeneration were available in one instrument.

3) Promised a mechanism for developing direct measurement of thermal reactions unique to thermal regeneration of activated carbon.

SECTION 9

METHODS, MATERIALS, AND PROCEDURES

In accordance with the objectives of this study, DTA was employed to detail selected sorbate uptake and experimental determination of thermal regeneration. The general plan of study developed for this investigation consisted of a series of broad range preliminary exploratory determinations followed by narrow range definitive determination. The first portion of the study was directed towards developing qualitative data relevant to DTA response and the thermal regeneration response of activated carbon sorbed materials.

The activated carbon used in this study was Filtersorb 400*. This material was initially applied in granular form, however analysis of this material required that the grain size be reduced to about 40 mesh. This factor was established by comparing the DTA thermograms developed by various sized grains of Filtrasorb 400. Results of this study showed that granular activated carbon ≃ 1/8 - 3/10" size produced a variable geometry in the DTA sample holders which resulted in spurious response. The sample cups employed in this study were capable of containing 5 and 50 mg of activated carbon. The relatively small size required that homogenous small grained sample materials be used. On the basis of this finding a modified method of sorption contact was developed using a thin film of 40 mesh activated carbon.

In order to develop quantitative data relative to DTA response, a series of organic materials were employed as standards and the appropriate peak area for selected endothermic-exothermic reactions were measured. The selected organic materials were benzoic acid, phenol and methylene blue. These materials were selected on the basis of established thermal standard characteristics, sorption affinity for activated carbon and analytical chemistry

response. Benzoic acid is a primary standard employed in calorimetry; whereas, methylene blue and phenol are readily sorbed by activated carbon and their concentration can be determined by colorimeteric or spectro-photometric analysis.

DTA was initiated by exploring the thermal characteristics of activated carbon. The apparatus selected for this work was a Model 202 DTA system manufactured by the R. L. Stone Company*. This system was equipped with 3/8" diameter 1/2" deep cylindrical nickel sample holders equipped with internal contact thermocouples and a 1/4" diameter 0.010" thick platinium disk sample holder supported on position indexing ring thermocouples. Each of the sample holders were placed in a pressure furnace module equipped with water cooling coils. A diagram of the thermocouples and furnace units are shown in Figure 28. This instrument was also equipped with a variable heating rate programmer, temperature limit switch and XY data plotter. The furnace unit for this instrument was constructed as a pressure vessel and used for low and high pressure applications.

Preliminary testing of the DTA system showed that activated carbon samples exhibited exothermic peaks in the 500-700^{o}C region when an inert gas, argon at 20 psi gauge, was used. Further study showed that the exothermic peak (evidence of combustion) was also produced under evacuated pressure conditions (10 mm Hg). Experimental evaluation of this situation showed that the exothermic peak formation could be eliminated by increasing the low pressure (10 mm Hg) degassing period to 30 minutes or by employing three five-minute serial pruges of the furnace with argon. During the course of this preliminary study a variety of activated carbon samples representative of several trade names were subjected to DTA to determine if the persistent exothermic reaction was related to the product or manufacturing process. Results of the study, Figure 29, showed that the exothermic reaction was common to all samples. Since low pressure degassing and pruging eliminated

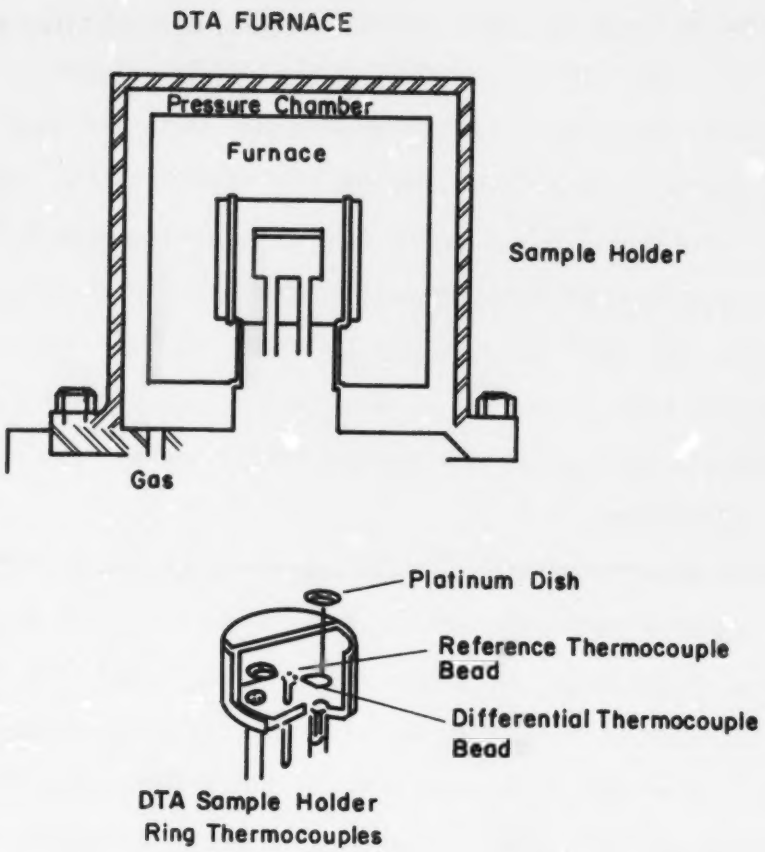

Figure 28. Diagram of DTA apparatus

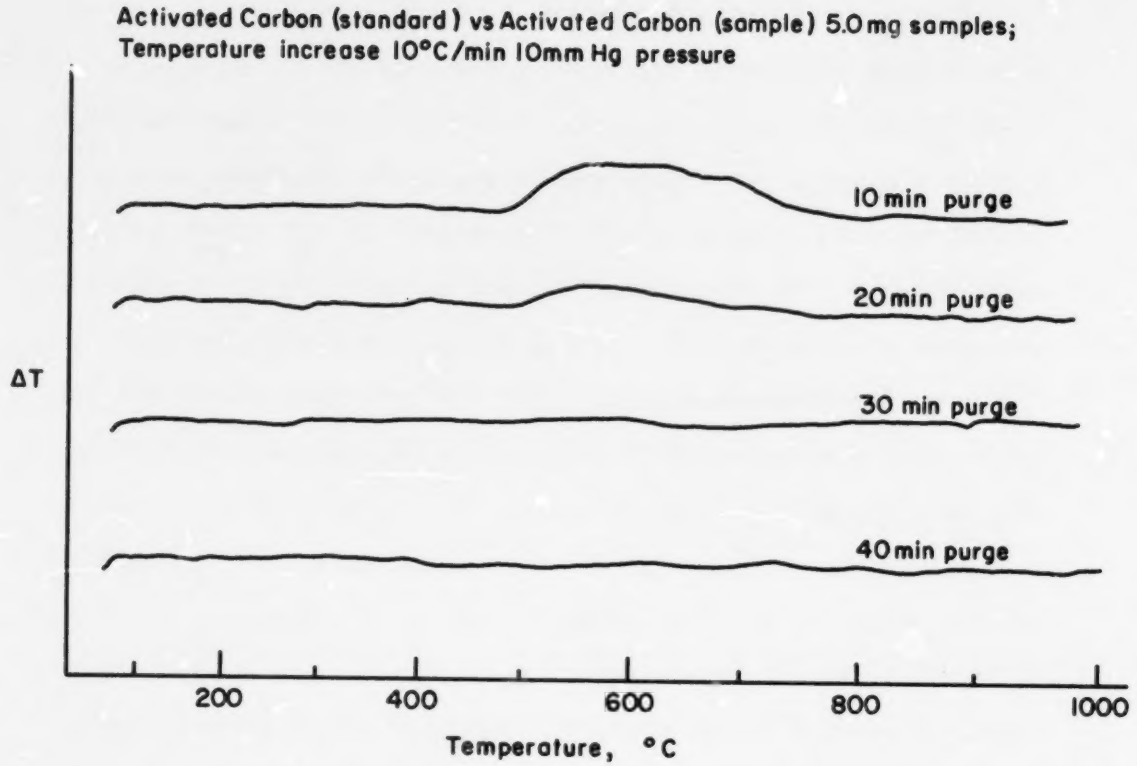

Figure 29. Effect of low pressure (10 mm Hg) degassing period on high temperature exothermic reaction of activated carbon.

the problem it seems likely that sorbed oxygen was released from the activated carbon in the 500-700^{o}C range. The balance of DTA work conducted in this study used either a preliminary 30 minute 10 mm Hg pressure degassing period for low pressure determinations or three 5 minute duration purges with Argon gas.

Qualitative thermal characteristics of activated carbon were determined under differential thermal conditions using a variety of sample materials, thermal standards and heating rates. Initially, basic standard materials such as aluminum oxide, silicon dioxide and quartz flour were employed as thermal reference standard materials in conjunction with virgin activated carbon samples. The objective of this exploratory study was to determine the baseline characteristics of the activated carbon under low pressure and inert atmosphere heating regimes. Results of this study showed that the standard reference materials provided conditions requisite to achievement of a well defined flat baseline; however, the standard thermal materials such as aluminum oxide, silicon dioxide and quartz flour diminished the sensitivity of the system to exothermic-endothermic responses. Further experimentation showed that the system of using virgin activated carbon as a thermal standard in conjunction with a sample of virgin activated carbon produced a relatively smooth baseline. In this arrangement the small differences in sample composition, grain size etc. were diminished and differences in thermal characteristics are recorded directly. Additional experimental study showed that the activated carbon (standard) vs. activated carbon (sample) system was the most sensitive on the basis of peak height response per unit mass of material. Moreover this system was most realistic for this study since the thermal energy difference between virgin activated carbon, organic sorbed activated carbon and regenerated activated carbon could be determined directly.

Following determination of baseline development and sample response, a systematic study of sample geometry and heating rate effects on repsonse was completed. Results of this study showed that the small sample (≃ 3 to 8 mg) located on the 1/4" diameter platimium foil crucibles - ring thermocouple sample holders provide optiminium qualitative response; whereas, the 3/8" diameter 1/2" deep nickel crucibles - contact thermocouples sample holders provided the most consistent quantitative response. Direct comparison of low pressure thermograms for various samples of activated carbon and organic materials showed that heating rates ranging from 10 to 12^{o}C per minute were necessary for this work.

Evaluation of the quantitative nature of the DTA method and apparatus was accomplished by determining the relative peak area developed by various sized samples of benzoic acid. Results of this determination are shown in Figure 30.

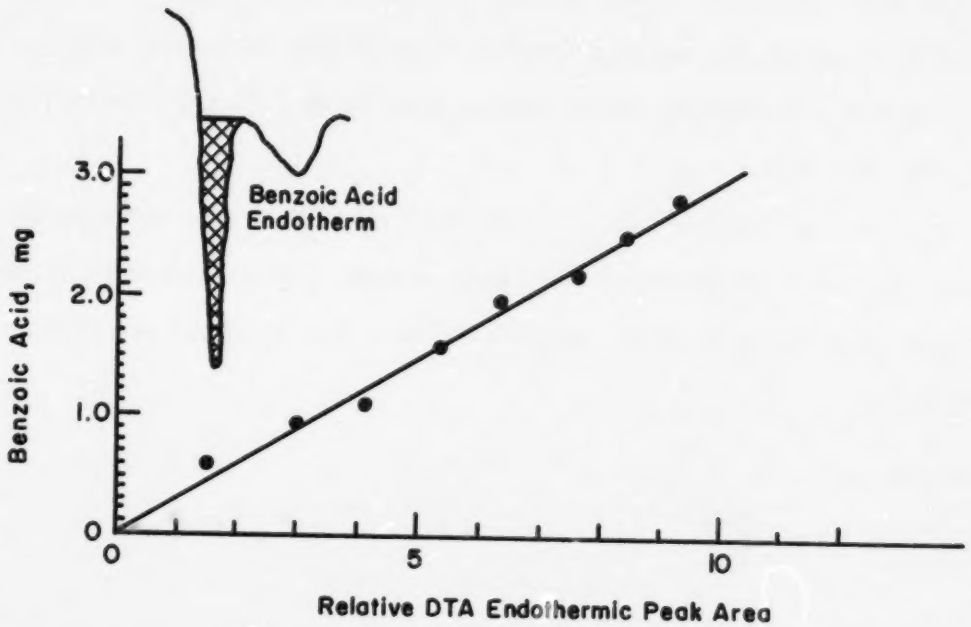

Figure 30. Quantitative response of DTA - bassed on benzoic acid standard.

SECTION 10

RESULTS

The broad range exploratory studies directed toward determining the factors affecting differential thermal analysis of activated carbon showed that sample grain size, sample preparation and heating rate were the dominant factors. Specifically the results of this study showed that:

1) activated carbon samples must be reduced to 40 mesh grain size
2) activated carbon samples must be degassed for 30 minutes at 10 mm Hg pressure prior to differential thermal analysis and
3) a minimum heating rate of $10^{o}C$/min and maximum of $15^{o}C$/min was necessary.

Experimental study of the thermal characteristics of phenol sorbed activated carbon produced a typical response pattern shown in Figure 31. Specifically the phenol-activated carbon shown in Figure 31 indicated that the phenol sorbate produced a sharp well defined endothermic peak in the 300-310^{o}C range. The characteristic endothermic pattern produced by phenol remained very nearly constant and demonstrated that the phenol was removed from the activated carbon in the 300-310^{o}C range.

Further study of the phenol-activated carbon thermal disassociation characteristics by DTA showed that the 300-310^{o}C region was the threshold temperature for thermal regeneration. This feature was established by measuring the sorption uptake of phenol following thermal regeneration of spent (phenol sorbed) samples of activated carbon. The response of this system in terms of sorption uptake vs. regeneration temperature values plotted in Figure 32 show that sorption regeneration remains at a constant low value in the 23^{o}C to 110^{o}C temperature range and increased linearly with temperature to the 310^{o}C region, thereafter it remained constant to about 500^{o}C.

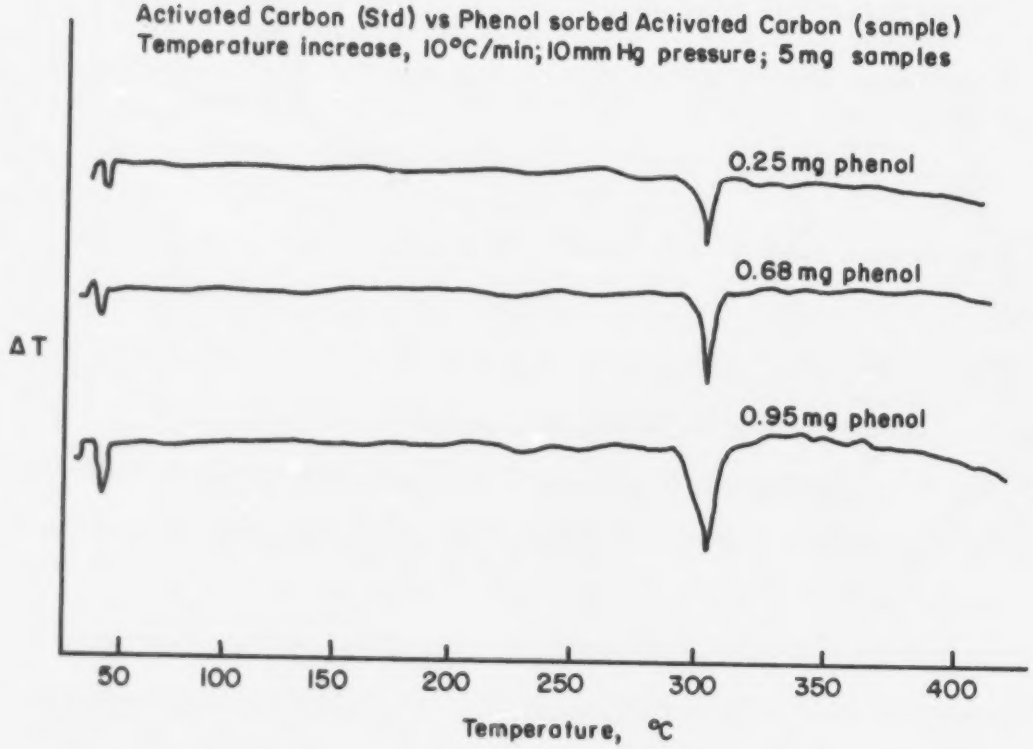

Figure 31. Phenol sorbed activated carbon DTA thermogram.

Temperatures greater than 500°C reduced the regeneration sorption capacity. Also shown in Figure 32 are the results of a temperature equilibrium study of phenol sorbed-activated carbon thermal regeneration. In this study phenol-sorbed activated carbon was heated to a selected temperature value and held at this value for 10 minutes. Results of this study plotted in Figure 32 showed a similar response to the continuous DTA results.

The most interesting feature of the DTA thermal regeneration study is the relatively high temperature required for thermal regeneration. Pure phenol is a solid at room temperature and exhibits a broad range melting point at about 42-43°C and a sharp boiling point at 181.5°C. Moreover phenol exhibits a relatively high vapor pressure and is a deliquiesent matertial. On the basis of these characteristics, if phenol were weakly sorbed to activated carbon it would be expected to be displaced from the activated carbon sorbent at some temperature value close to phenol boiling point value. At a low pressure value of 10 mm Hg, the boiling point value for phenol is 73.5°C; significantly less than the 310°C value determined by the DTA study.

Experimental study of the high temperature characteristics of activated carbon sorbed phenol by DTA established that the temperature ranges determined in the thermal regeneration were realistic. Experimentation with various sized samples of phenol and phenol sorbed activated carbon verified the boiling and melting point values for pure phenol and showed that activated carbon sorption displaced the melting point endotherm pattern from 182 to 310°C.

This finding suggests that the amount of thermal energy requisite to thermal regeneration of phenol sorbed activated carbon might be proportional to the temperature difference between the boiling point for pure phenol and the threshold thermal regeneration point. Verification of this relationship was considered to be beyond the scope of this study and further study of this relationship is required.

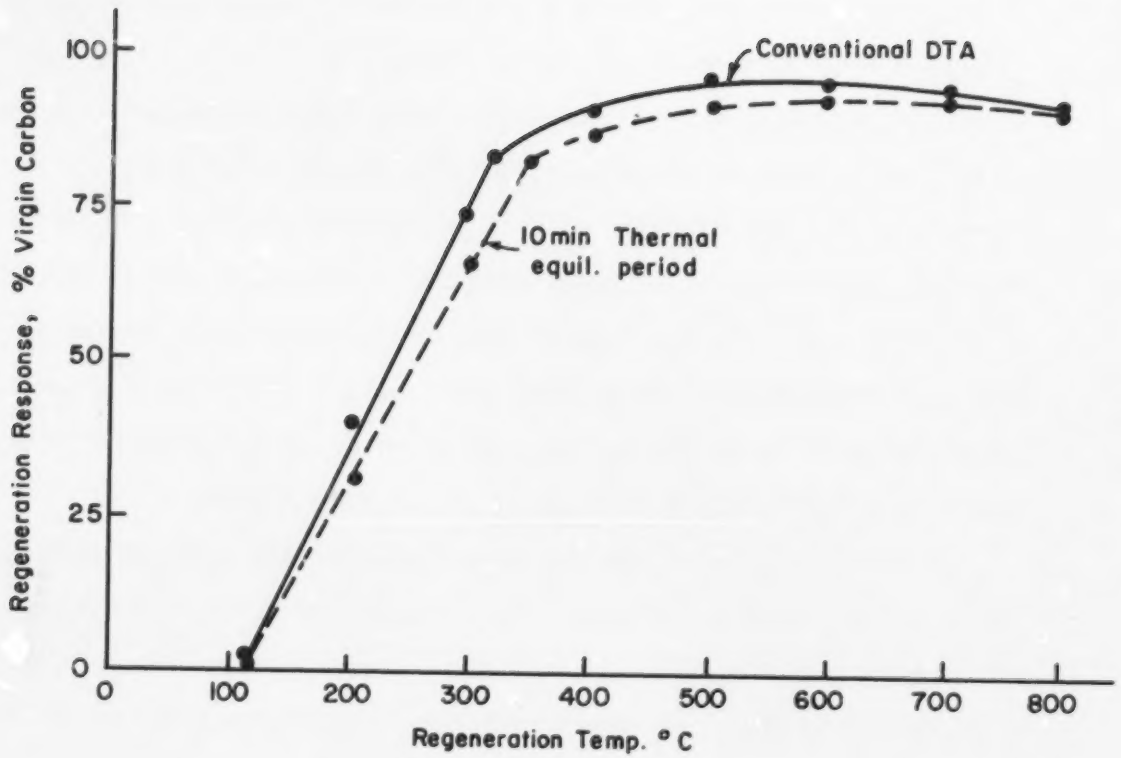

Figure 32. Regenerated sorption capacity developed by DTA study of phenol-activated carbon system.

Experimental study of the methylene blue-activated carbon system showed a thermal response pattern somewhat similar to the phenol sorbed activated carbon thermal regeneration study. The significant exceptions were; 1) methylene blue did not exhibit a sharp melting point rather it decomposed on heating, 2) Methylene blue thermograms developed by low pressure (10 mm Hg) heating exhibited broad exothermic patterns similar to the curve shown in Figure 33. Samples of methylene blue sorbed activated carbon subjected to low pressure (10 mm Hg) and evaluated for sorption uptake, Figure 34, yielded thermograms similar to the curves shown in Figure 33. As in the phenol sorbed-activated carbon regeneration study, the threshold temperature of methylene blue thermal decomposition determined by DTA established the lower limit temperature for thermal regeneration. This factor was reevaluated independently during the course of the thermal regeneration study of methylene blue-activated carbon system. Results of the DTA thermal regeneration study, shown in Figure 34, predict that thermal regeneration in the 100^{o}C to 800^{o}C region would progress exponentially. Plotted values in Figure 34 also showed that thermal regeneration above 800^{o}C was not effective in restoring sorption capacity. Generally the efficiency of sorption regeneration as a function of temperature yields a response directly proportional to the thermal reaction curve derived from activated carbon-methylene-blue sorbed carbon was significantly different from phenol sorbed carbon.

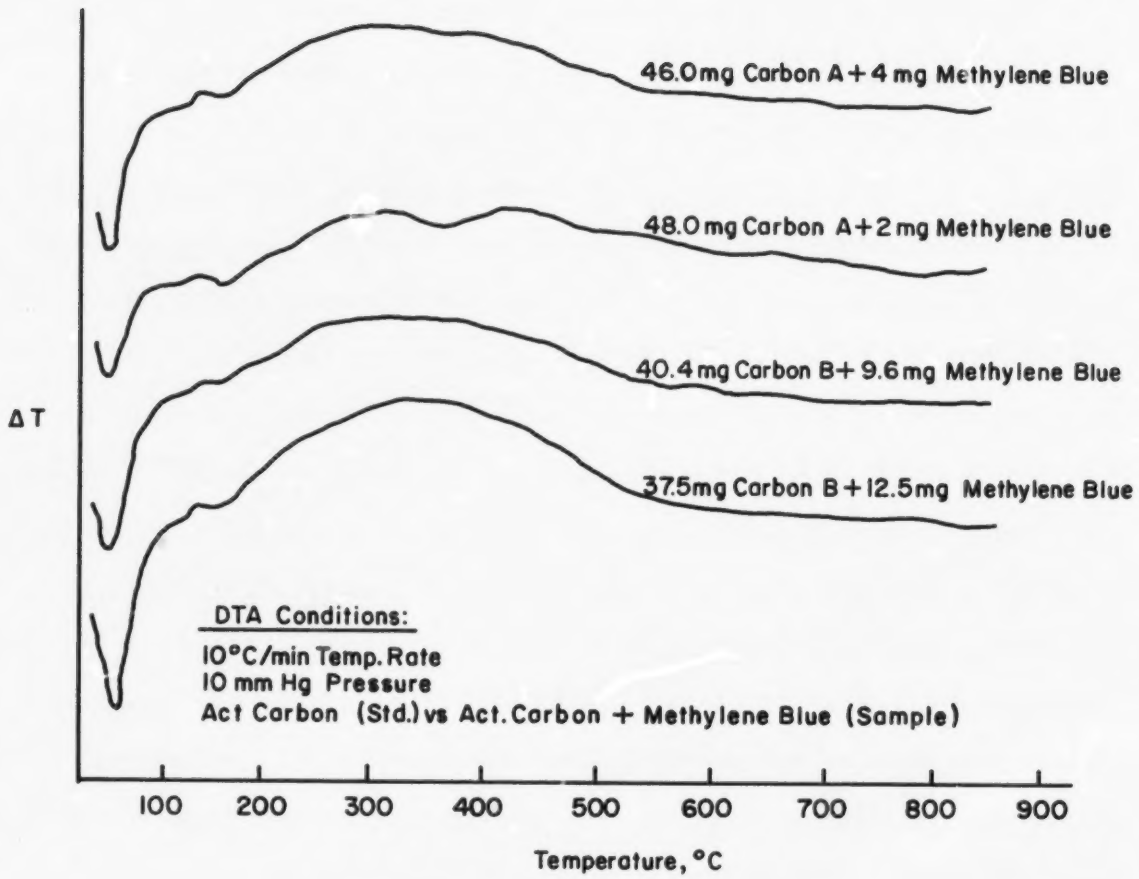

Figure 33. Methylene blue sorbed activated carbon DTA thermogram.

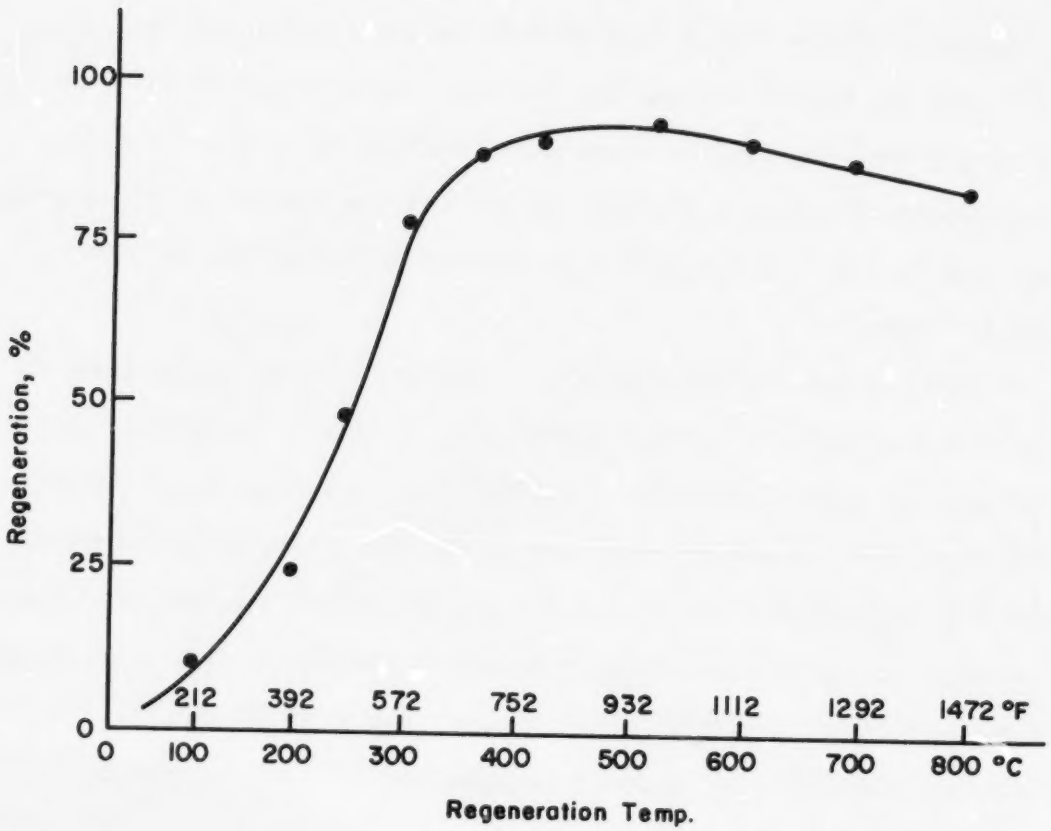

Figure 34. Regenerated sorption capacity developed by DTA study of methylene-blue activated carbon system.

SECTION 11

SUMMARY

Results of the DTA study of thermal regeneration of activated carbon under low pressure conditions showed that DTA is a realistic and promising tool for detailing qualitative and quantitative regeneration response.

Comparison of the results derived from the DTA study of thermal regeneration with the results derived from the bench scale vacuum regeneration study showed that the sorption regeneration response was similar and that the temperature limits were similar. In addition the results of both studies showed that various sorbates exhibit unique thermal properties and require systematic study.

Potentially DTA provides a method for studying thermal regeneration on a direct determination of sorbent uptake capacity basis. Tentatively this method could be used to determine specific temperature response of thermal regeneration as a function of sorption loading or pre-treatment conditions. The direct application of DTA to the analytical problems involved in activated carbon sorption and thermal regeneration require careful consideration of the sorbate and probable conditions. Optimum utilization of DTA for this purpose may require development of special techniques and DTA instrumentation.

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